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New considerations for PM, Black Carbon and particle number concentration for air quality monitoring across different European cities

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Abstract. In many large cities of Europe standard air quality limit values of particulate matter (PM) are exceeded. Emissions from road traffic and biomass burning are frequently reported to be the major causes. As a consequence of these exceedances a large number of air quality plans, most of them focusing on traffic emissions reductions, have been implemented in the last decade. In spite of this implementation, a number of cities did not record a decrease of PM levels. Thus, is the efficiency of air quality plans overestimated? Do the road traffic emissions contribute less than expected to ambient air PM levels in urban areas? Or do we need a more specific metric to evaluate the impact of the above emissions on the levels of urban aerosols?

This study shows the results of the interpretation of the 2009 variability of levels of PM, Black Carbon (BC), aerosol number concentration (N) and a number of gaseous pollutants in seven selected urban areas covering road traffic, urban background, urban-industrial, and urban-shipping environments from southern, central and northern Europe.

The results showed that variations of PM and N levels do not always reflect the variation of the impact of road traffic emissions on urban aerosols. However, BC levels vary proportionally with those of traffic related gaseous pollutants, such as CO, NO_2 and NO. Due to this high correlation, one may suppose that monitoring the levels of these gaseous pollutants would be enough to extrapolate exposure to traffic-derived BC levels. However, the BC/CO, BC/NO_2 and BC/NO ratios vary widely among the cities studied, as a function of distance to traffic emissions, vehicle fleet composition and the influence of other emission sources such as biomass burning. Thus, levels of BC should be measured at air quality monitoring sites.

During morning traffic rush hours, a narrow variation in the N/BC ratio was evidenced, but a wide variation of this ratio was determined for the noon period. Although in central and northern Europe N and BC levels tend to vary simultaneously, not only during the traffic rush hours but also during the whole day, in urban background stations in southern Europe maximum N levels coinciding with minimum BC levels are recorded at midday in all seasons. These N maxima recorded in southern European urban background environments are attributed to midday nucleation episodes occurring when gaseous pollutants are diluted and maximum insolation and O_3 levels occur. The occurrence of SO_2 peaks may also contribute to the occurrence of midday nucleation bursts in specific industrial or shipping-influenced areas, although

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at several central European sites similar levels of SO_2 are recorded without yielding nucleation episodes.

Accordingly, it is clearly evidenced that N variability in different European urban environments is not equally influenced by the same emission sources and atmospheric processes. We conclude that N variability does not always reflect the impact of road traffic on air quality, whereas BC is a more consistent tracer of such an influence. However, N should be measured since ultrafine particles (<100 nm) may have large impacts on human health.

The combination of PM_{10} and BC monitoring in urban areas potentially constitutes a useful approach for air quality monitoring. BC is mostly governed by vehicle exhaust emissions, while PM_{10} concentrations at these sites are also governed by non-exhaust particulate emissions resuspended by traffic, by midday atmospheric dilution and by other non-traffic emissions.

1 Introduction

Health impact of ultrafine particles (UFP) has motivated a great deal of ambient aerosol research in recent years. Several studies suggest that UFP disproportionately induce oxidative stress in cells and are more toxic compared to larger particles of similar composition (Li et al., 2003; Nel et al., 2005). Research studies have indicated that fine particles may be more toxic because a large proportion of these particles are derived from traffic-related, industrial, and domestic emissions which contain abundant transition metals (Anderson et al., 2001; Klemm et al., 2000; Schwartz et al., 2002; von Klot et al., 2002). Furthermore, UFP have also been suggested to be more toxic because of the large surface area available for biologic interactions with lung cells (Chio et al., 2008). Epidemiological studies (Akinson et al., 2010; Stolzel et al., 2007) have shown a clear association of urban nanoparticle exposures with adverse cardiovascular health outcomes.

Because of the low influence of UFP on PM mass concentration (the current metric used in European air quality legislation), the number concentration (N) can be a better descriptor of the variability of UFP. In fact, the combination of number and size distribution of N may elucidate on the primary or secondary production of these UFP.

In many large cities of Europe standard air quality limit values of PM are exceeded. Emissions from road traffic and biomass burning are frequently reported to be the major causes of such exceedances (EEA, 2010). As a consequence of these exceedances a large number of air quality plans, most of them focusing on traffic emissions, have been implemented in the last decade. In spite of this implementation, a number of cities did not record a decrease of PM levels. Thus, the question remains: is the efficiency of air quality plans overestimated? Do the road traffic emissions contribute less than expected to ambient air PM levels in urban areas? Or do we need a more specific metric to evaluate the impact of the above emissions on the levels of urban aerosols?

A number of studies have reported a strong association between BC and road traffic (Hamilton and Mansfield, 1991; Watson et al., 1994; Pakkanen et al., 2000) and biomass burning (Sandradewi et al., 2008) emissions. While BC aerosols are not the only cause of adverse health effects due to particles, they are a major factor, specially the ultrafine BC. Indeed, the recent WHO report concludes that "combustion-derived aerosols are particularly significant in terms of their health effects" (WHO, 2003).

On the other hand, number concentrations in urban areas are also highly influenced by primary vehicle exhaust emissions (Morawska et al, 2002; Bukowiecki et al., 2003; Hueglin et al., 2006; Rodriguez and Cuevas, 2007, Pérez et al., 2010). These emissions show bimodal size distribution, with a nucleation mode below 30 nm and a carbonaceous mode peaking between 50–130 nm (Morawska et al., 1998, Casati et al., 2007). Therefore, a number of studies pointed out that exposure to road traffic emissions may be properly evaluated by combining ambient air measurements of Black Carbon (BC) with N concentrations (Fischer et al., 2000; Harrison et al., 2004; Janssen et al., 1997; Smargiassi et al., 2005; Rodriguez and Cuevas, 2007), since nowadays these parameters seem not to be properly controlled by air quality limit values.

Although most of UFP in urban atmospheres are related to vehicle exhaust emissions, its origin may be both primary and secondary (Wehner et al., 2002; Dunn et al., 2004; Van Dingenen et al., 2004). Gaseous pollutants from vehicle exhaust may yield a high aerosol production depending on the ambient air conditions. For example, Casati et al. (2007) observed that low ambient temperature and high relative humidity favour secondary formation processes, while Shi and Harrison (1999) associated these processes with high dilution after the emission. Furthermore, Wehner et al. (2009) reported evidence on the fact that under high engine load conditions a favourable setting for secondary particle formation is given within short distance of the exhaust plume. Such conditions (e.g., acceleration) are typical of urban driving. These particles in the vehicle exhaust mainly comprise organic compounds and sulphuric acid and are frequently one of the most important fractions in terms of number concentration (Kittelson et al., 1998).

New secondary particle formation in ambient air is mostly attributed to nucleation and cluster/particle growth by condensation of photo-oxidised vapours (Morawska et al., 2008; Dunn et al., 2004) occurring some time after the emission (hours to days). The outcome of UFP depends widely on the pollutants concentrations in the air, thus when the urban atmosphere is highly polluted, the semi-volatile species condense onto pre-existing particles (Wichmann et al., 2000; Zhang et al., 2004; Imhof et al., 2006); however, when low

PM pollution levels occur, the semi-volatile species may result in large numbers of nucleation-derived aerosols (Hämeri et al., 1996; Rönkkö et al., 2006). As previously reported, urban areas with high solar radiation intensities are favourable scenarios for nucleation processes (Johnson et al., 2005; Moore et al., 2007; Pey et al., 2008, 2009; Fernández-Camacho et al., 2010; Cheung et al., 2010). Elevated solar radiation intensities not only provide enough energy for gaseous precursors to nucleate, but favour the dilution processes as a result of the growing of the mixing layer and the activation of mountain and sea breezes. In case of coastal cities, such as Barcelona and Santa Cruz de Tenerife, the significant SO_2 emissions from shipping may be transported towards the city with the sea breeze, enhancing the nucleation processes. The combination of the oxidation products of SO_2 and VOCs are ideal for efficient nucleation (Metzger et al., 2010).

Once created, nucleated particles may undergo different processes in the atmosphere (Boy and Kulmala, 2002; Qian et al., 2007; Park et al., 2009; Gao et al., 2009; Cheung et al., 2010): (1) burst of nucleation particles without subsequent growth into larger particles, and (2) nucleation coupled with growth. Factors governing the evolution of nucleated particles without subsequent growth are not well-documented (Johnson et al., 2005; Moore et al., 2007; Pey et al., 2008; Park et al., 2009; Gao et al, 2009) and further research is needed to elucidate the occurrence of this process in urban environments. At coastal urban sites, the development of sea breezes (enriched in SO_x) simultaneously with the highest solar radiation could be probably related with this process. Both factors favor nucleation processes, but the significant increase in wind speed can be responsible for a high dilution of the condensable gases involved in growth. Thus, studies have confirmed that the growth rate depends on temperature and concentration of available condensable vapors (Kulmala et al., 2004). In some cases it has been suggested that H_2SO_4 condensation typically accounts for about 10–30 % of the observed growth (Weber et al., 1997; Boy et al., 2005), whereas VOCs account for more than 70 % of the material for the particle growth.

The daily cycle of N evidences significant differences when comparing cities with distinct meteorological conditions. Daily N cycles showing new particle formation coinciding with sea breezes blowing inland have recently been observed in the urban background of coastal cities in south-western Europe, such as Barcelona, Santa Cruz de Tenerife and Huelva (Pey et al., 2008; Rodríguez et al., 2008; Fernández-Camacho et al., 2010; Pérez et al., 2010), as well as in Brisbane, Australia (Mejia et al., 2009; Cheung et al., 2010). In other cases such as Beijing, daily formation of nucleation mode particles was coincident with the arrival of cleaner air masses (Zong-bo et al., 2007).

The increase in knowledge of UFP has not been accompanied by more in-depth research about the main factors governing differences in the secondary formation of particles between urban sites under a variety of emission sources and climate/geographic conditions. In this context, the main goal of this paper is to study the causes responsible for the variability of levels of N, BC, PM and gaseous pollutants at a selection of air quality monitoring sites representative of different climate zones and urban environments in Europe, with especial focus on the process of formation of secondary UFP with high influence on the variability of N.

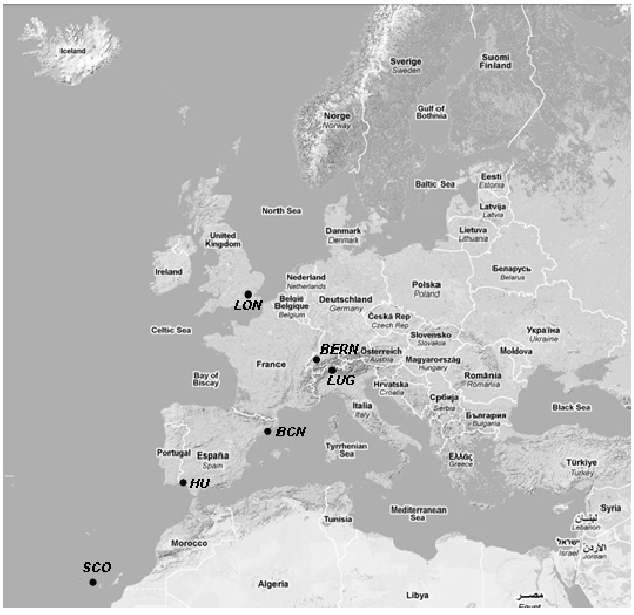

Fig. 1. Location of the six cities selected in the present study.

2 Monitoring sites

Seven monitoring sites situated in six major European cities (Fig. 1) with different climatic and meteorological patterns were selected for the study. The selection of the cities/sites intended to cover different climatic zones across Europe (central, western and southern Europe), as well as urban environments (urban background and traffic, urban-industrial and urban-shipping-influenced sites). The following sites also cover a relatively wide range of road traffic density, urban architecture and fleet composition (Table 2):

- A southern-European urban background site (Barcelona, BCN) characterized by a very dense road traffic network, but also by the influence of industrial and shipping emissions.
- A north-European urban background site (North Kensington, UK, NK) in the grounds of a school in a residential area 7 km to the west of central London.
- Two urban traffic sites situated directly at the kerbside of very busy roads: Bern (Switzerland, central-Europe),

with a traffic density of 25 000 vehicles/day, and Marylebone road in London (UK, northern-Europe), with a traffic density of 80 000 vehicles/day.

- A central-European urban background site (Lugano, Switzerland, LUG) situated in a park in the south of the Alps.
- A southern-European urban background site (Huelva, HU) highly influenced by the emissions from a large industrial estate including copper metallurgy, petrochemical and fertilizing plants.
- A subtropical island urban background site (Santa Cruz de Tenerife, Spain, SCO) on the western side of a 4-lane road running along the shore, with influence of the emissions from a nearby large harbour and an industrial-petrochemical estate.

2.1 Barcelona, BCN (urban background site in a city with dense traffic)

Barcelona is located in north eastern Spain (41° 23′ 05° N; 02° 07′ 09° E; 68 m a.s.l.), in the western Mediterranean Basin. It is the tenth most populous city in Europe, with about 1.7 million inhabitants. The urban architecture and dynamism around Barcelona account for the highest road traffic density of Europe (6100 cars km^{-2}, much more than in most European cities with 1000–1500 cars km^{-2}). As shown in Table 1, Barcelona is characterized by a high proportion of diesel cars, motorbikes, heavy duty vehicles, and a large proportion of the use of private cars for the daily mobility. Furthermore, Barcelona has one of the main harbours in the Mediterranean Basin, with the highest number of cruise ships for tourists in Spain, being a significant focus of emissions of atmospheric pollutants, which are very often transported across the city by sea breeze. Finally, a wide range of intensive industrial activities, three natural gas power stations and two city waste incinerators are also based in the metropolitan area.

In addition to the local PM emissions, Saharan dust outbreaks reach the Barcelona area in the order of 7–10 events per year, with a major frequency in the summer and winter–spring periods (Rodríguez et al., 2001).

The transport and dispersion of atmospheric pollutants within BCN are controlled mainly by fluctuating coastal winds which typically blow in from the sea during the day and, less strongly, from the land during the night. The sea breezes (originating from the 120–180° sector) are at their strongest around midday, when the boundary layer height maximizes (Pérez et al., 2004). The average annual solar radiation is 180 W m^{-2} and at midday values range between 400 and 950 W m^{-2} within a whole year. The annual accumulated precipitation is 500 mm.

Measurements were carried out at an urban background monitoring site located in southwest Barcelona, being influenced by vehicular emissions from one of the city's main traffic avenues, located at approximately a distance of 300 m with a mean traffic density of 132 000 vehicles/day. Thus, the site is an urban background one, but it is located in a city with very high road traffic, and influenced by the emissions of one of the largest arterial roads of the city.

2.2 London (urban background and traffic sites)

London has a population of 7.6 million, whilst the Greater London metropolitan area has between 12.3 and 13.9 million, making it the largest in the European Union (Wikipedia, 2010). The traffic density in London in 2009 was 1317 registered vehicles km^{-2} of which 1134 km^{-2} were cars. As shown in Table 1, London is characterized by a lower proportion of diesel cars, motorbikes, heavy duty vehicles, and also low proportion of the use of private cars for the daily mobility.

On an annual basis, mean solar radiation is 70 W m^{-2}, with values ranging from 5 to 760 W m^{-2} at midday. The daily pattern of the boundary layer height shows maximum from 12:00 to 15:00 UTC, contributing to decrease atmospheric pollutants concentration.

For the present study two air quality monitoring sites were selected:

2.2.1 London, Marylebone, MR (urban traffic site)

The London–MR monitoring site is located on the kerbside of a major arterial route in London that is heavily trafficked (51°31′ 96° N; 00°9′ 55″W; 27 m a.s.l.). The surrounding area is a street canyon frequented by pedestrians because of tourist attractions and shops. High PM_{10} concentrations are measured at MR and the permitted number of days with concentrations above the limit value was exceeded in 2005. This site is classified as a roadside site. The MR supersite belongs to the London Air Quality Network. The surrounding buildings form an asymmetric street canyon (height-to-width ratio of about 0.8). Traffic flows of over 80 000 vehicles/day pass the site on six lanes with frequent congestion. Braking is frequent near the measurement site due to the presence of traffic lights 50 m to the west and an intersection to the east. The instruments are in a cabin and sampling inlets are less than 5 m from the road. Local PM_{10} emissions are strongly dominated by the heavy-duty vehicles that represent less than 10 % of the traffic (Charron and Harrison, 2005).

2.2.2 London, North Kensington, NK (urban background)

This is sited in the grounds of Sion Manning School in St Charles Square, North Kensington (51° 31′ 16″ N; 00° 12′48″ W; 27 m a.s.l.), surrounded by a mainly residential area. The NK site is located about 4 km to the west of MR site.

Table 1. Features of fleets and commuting of the 6 selected cities.

	Barcelona	London	Bern	Lugano	Huelva	Sta. Cruz
% Diesel fleet	45[a]	?	17[d]	17[d]	55[a]	24[a]
% New cars diesel	70[a]	33[c]	30[d]	27[d]	?	?
Commuting						
Private car	40[b]	37[c]	35[e]	48[f]	45[g]	?
Public T.	28[b]	41[c]	18[e]	12[f]	1[g]	?
Pedestrian	32[b]	21[c]	47[e]	40[f]	52[g]	?
Fleet						
Motorbike	29[b]	4[c]	18[e]	16[f]	7[g]	6[g]
Passenger and LDV	63[b]	93[c]	77[e]	81[f]	87[g]	87[g]
Bus	2[b]	1[c]	1[e]	1[f]	0.2[g]	0.4[g]
HDV	3[b]	1[c]	1[e]	1[f]	3[g]	4[g]
Other	2[b]	1[c]	3[e]	2[f]	1[g]	2[g]

[a] Dirección General de Tráfico, Spain: http://apl.dgt.es/IEST2.

[b] Baldasano et al. (2007).

[c] Department of Transport, UK: http://www.dft.gov.uk.

[d] Swiss Federal Statistical Office: http://www.bfs.admin.ch.

[e] Ecoplan (2007) Auswertung Mikrozensus 2005 für den Kanton Bern, Report, Bern:
http://www.bve.be.ch/bve/de/index/mobilitaet/mobilitaet_verkehr/mobilitaet/grundlagen_mobilitaet.html.

[f] www.tiresia.ch.

[g] Oral communications from local councils.

Table 2. Main information about the monitoring sites selected for the study.

	Longitude	Latitude	Altitude (m a.s.l.)	Station type
Barcelona (ES)	02° 07′ 33″ E	41° 23′ 55″ N	80	Urban background
Lugano (CH)	08° 57′ 26″ E	46° 00′ 40″ N	281	Urban background
North Kensington (London, UK)	00° 12′ 48″ W	51° 31′ 16″ N	27	Urban background
Bern (CH)	07° 26′ 27″ E	46° 57′ 04″ N	536	Urban traffic
Marylebone Road (London, UK)	00° 09′ 55″ W	51° 31′ 96″ N	27	Urban traffic
Huelva (ES)	05° 56′ 24″ W	03° 15′ 21″ N	10	Urban industrial
Santa Cruz de Tenerife (ES)	16° 18′ 33″ W	28° 29′ 20″ N	52	Urban background

2.3 Bern, Bern (urban traffic site)

Bern is a city with a population of 0.125 million and the fourth most populous city in Switzerland. The urban area of Bern including neighbouring communities has a population of 0.35 million. Bern is the capital of Switzerland and the Canton of Bern. The city is located north of the Alps in the Swiss plateau (46° 57′ 03″ N, 07° 26′ 27″ E, 536 m a.s.l.). Attending to the typical meteorological feature, the mean annual solar radiation is 130 W m^{-2} and it ranges from 15 W m^{-2} in winter to 840 W m^{-2} in summer at noon. The accumulated precipitation in the city is about 1700 mm per year. The monitoring site is located in a busy street canyon in central Bern (20 000–30 000 vehicles/day). The economy of Bern is dominated by public authorities and small and medium sized enterprises from different sectors. There are, however, no major industries with especially high emissions or air pollutants. As shown in Table 1, Bern is characterized by a low proportion of diesel cars and heavy duty vehicles, high proportion of motorbikes.

2.4 Lugano, LUG (urban background site)

Lugano is a city with 55 000 inhabitants and a total of 145 000 people living in Lugano and the neighbouring community. The city lies at the edge of Lake Lugano at the southern foothills of the Alps (46°00′ 40″ N, 08° 57′ 26″ E, 281 m a.s.l.) and is surrounded by three mountains with

elevations of around 1000 m a.s.l. As shown in Table 1, Lugano is characterized by a low proportion of diesel cars and heavy duty vehicles and a high proportion of motorbikes. There are no major important industrial sources of air pollutants within the close vicinity of Lugano. However, Lugano lies close to the Italian border and is strongly influenced by emissions from the Lombardy region.

Precipitations are frequent, with an accumulated value of 3800 mm per year. Mean solar radiation is 150 W m^{-2} on average, at midday this parameter is between 3 and 900 W m^{-2}.

The measurement site in Lugano represents an urban background situation. The site is located on campus of the University of Lugano in the city center. About 50 m to the east is a busy urban road (CorsoElvezia), buildings protect the site from direct road traffic emissions towards all other wind directions.

2.5 Huelva, HU (urban background site influenced by industrial emissions)

Huelva is located south western Spain (37° 15′ 0° N, 6° 57′0° W, 54 m a.s.l) and has a population of around 0.15 million. In addition to the typical urban emissions (with a high proportion of diesel cars), aerosol precursors are emitted at the south of the city, where two large industrial estates are located: Punta del Sebo and Nuevo Puerto, both near the harbor of Huelva. The Punta del Sebo Industrial Estate includes the second smelter factory in Europe, where SO_2, H_2SO_4, As, Sb, Pb, Zn and Sn emissions are well documented. Phosphoric acid production plants are also installed in this industrial estate. NH_4^+ and Na phosphate, phosphoric acid, sulphuric acid and sodium silicate atmospheric emissions may be expected from these industrial activities. The most important air pollutant emissions in Nuevo Puerto occurs in a petroleum refinery, resulting in emissions of volatile hydrocarbons, SO_2, NO_x, NH_3, Ni and V. Shipping emissions occur also in the important industrial harbor of Huelva. In all these cases sea-to-land winds result in the inland transport of aerosols and their precursors (e.g. SO_2) affecting the city of Huelva.

The city of Huelva is also affected by natural PM contributions such as North African dust outbreaks, which produce a generalized increase in mass levels of particulate matter. The annual frequency of this natural phenomenon is calculated to be 19 % of days in southern Spain (Sánchez de la Campa et al., 2007). This area is characterized by a dry weather, with a yearly accumulated rainfall of 450 mm. The solar radiation is very elevated, reaching average values of 1200 W m^{-2} on an hourly basis at midday. The dispersion and transport of air pollutants in this area are highly influenced by the topographic settings. At night, the wind mostly blows from the north and during daylight, southern airflows linked to thermally driven breezes predominate. This sea breeze favors the entry of industrial plumes and is associated with an increase in ozone concentrations (Millán et al., 2002). The boundary layer height maximizes from 12:00–15:00 UTC.

Measurements were carried out at an urban background monitoring site placed at the University Campus, on the northeast corner of the city of Huelva, 7 km from Punta del Sebo and 14 km from Nuevo Puerto industrial areas. This monitoring station belongs to the air quality network of the Autonomous Government of Andalusia. The closest roads lie about 500 and 1000 m to the west and the east of the measurement site.

2.6 Santa Cruz de Tenerife, SCO (urban background site under the influence of shipping and industrial emissions)

Santa Cruz de Tenerife is a city with around 0.223 million population located in the Canary Islands – Spain (28°29′ 20′ N, 16°18′ 33″ W; 52 m a.s.l.). It is located at the bottom of the southern slope of the Anaga ridge and the eastern slope of the NE to SW ridge crossing the Island. This topographic setting protects the city from the trade winds (NNE) that blow over the ocean (Guerra et al., 2004). The main sources of pollutants in the city are: vehicle exhaust emissions (with a low proportion of diesel cars), emissions of ships and cargo operations in the harbour and an oil refinery located in the southern side of the city (Rodríguez and Cuevas, 2007; Rodríguez et al., 2008).

The urban scale transport of air pollutants in Santa Cruz de Tenerife is mainly driven by breeze circulation. This breeze is characterised by inland (westward) airflows during daylight (3–4 m s^{-1}) and a slight seaward (eastward) airflow at night (1 m s^{-1}). Inland breeze blowing starts at 08:00 UTC and is characterised by an abrupt shift in wind direction (Rodriguez et al., 2008). Solar radiation is 250 W m^{-2} on annual average, with a maximum of 1200 W m^{-2} at midday in summer, coinciding with the maximum height of the mixing layer.

Measurements were performed in the Santa Cruz Observatory. This is a coastal urban background site mainly influenced by vehicle exhaust and harbour emissions, and also by the emissions from a petrochemical estate. In addition to the local emissions, about 54 natural Saharan dust events occur along the year (Alonso-Pérez et al., 2007), often resulting in $PM_{10} > 100\,\mu g\,m^{-3}$ (Viana et al., 2002).

3 Instrumentation

Data on the instrumentation deployed at the different sites is summarized in Table 3. For the present study hourly averaged 2009 data were collected for each parameter and monitoring site.

It is relevant to note that differences in BC and N concentrations can be partly derived from the instrumentation. The latter were measured with a total of three models of

Condensation Particles Counters (CPC) which counted particles larger than 2.5 nm (TSI 3025 and TSI 3776), 5 nm (TSI 3785) or 7 nm (TSI 3022A). The use of CPCs with different cut sizes is likely to influence the results somewhat, as a largest cut size can imply an underestimation of N, resulting in lowest N/BC ratios.

As regards BC, the Multi-Angle Absorption Photometer (MAAP) (Thermo^{TM}, model Carusso 5012) instrument calculates absorbance from particles deposited on the filter using measurements of both transmittance and reflectance at two different angles. The absorbance is converted to the mass concentration of BC using a fixed mass absorption coefficient at 637 nm (Müller et al., 2010) of 6.6 $m^2\,g^{-1}$ recommended by the manufacturer. Nevertheless, experimental results showed average absorption coefficients of 9.2 $m^2\,g^{-1}$ in BCN, 12.1 in LUG, 10.9 in Bern, 10.3 in HU and 9.8 in SCO. Results were obtained by in situ determining elemental carbon (EC) for high volume samples of 24 h by means of the Thermo Optical Transmittance technique (Birch and Cary, 1996) using a Sunset Laboratory OC-EC analyser and the default temperature steps of the EUSAAR2 program (Cavalli et al., 2010). These experimental conversion factors were used in this study.

On the other hand, the Aethalometer (Magee AE 21) measured at 880 nm and a mass absorption cross section of 16.6 $m^2\,g^{-1}$ is recommended by the manufacturer to convert the observed light attenuation to the mass concentration of BC. In 2009, high correlation coefficients were obtained between BC mass and EC concentrations in North Kensington ($r^2 = 0.86$) and Marylebone (0.77) and the slope of the regression line was 0.97 and 1.19, respectively. Thus, the calculation of the experimental absorption coefficients, by means of the determination of EC, showed a value higher than the recommended one (16.6 $m^2\,g^{-1}$) in Marylebone (19.7) and closed to it in North Kensington (16.3).

Therefore, in order to perform an accurate comparison between sites, BC concentrations were determined using the experimental absorption coefficients (σ in $m^2\,g^{-1}$) according the equation by Petzold and Schönlinner (2004) (1):

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

where σ_{ap} are the absorption coefficient measurements in $M\,m^{-1}$.

Although the influence of possible coatings of BC particles by organic materials has not been taken into consideration, the correction of BC values with local EC concentrations carried out in this study favours the comparability between BC in the different cities. This influence could modify the N/BC ratios calculated in this work for the different periods of the day, but it would not alter the trends described.

On the other hand, in spite of this correction, the use of different instrumentations can still affect the seasonal trends of light absorbing carbonaceous aerosols. However, correlations between BC and EC measurements considering the whole year were significant in all the sites under study.

Regarding gaseous pollutants instrumentation, it is important to mention that NO_2 measurements can be overestimated because of interferences of oxidized nitrogen compounds in the conventional instruments equipped with molybdenum converters (Steinbacher et al., 2007).

4 Results and discussion

4.1 Levels of atmospheric pollutants

For the analysis and description of the trends observed for the different parameters, stations have been classified into three groups: (1) traffic stations (MR and Bern), (2) urban background stations (BCN, LUG and NK) and (3) urban background stations with special characteristics (industrial influence in the case of HU and subtropical island conditions, with the influence of shipping and industrial emissions, in the case of SCO). Table 4 lists the 2009 average values of the parameters measured in each station during the sampling period.

Average levels of PM_{10} range from 18 to 32 $\mu g\,m^{-3}$. As expected, the highest values (27–32 $\mu g\,m^{-3}$) were registered for kerbsides and also in the BCN urban background site, due to its proximity to one of the largest arterial roads of the city.

Levels of BC at urban background sites range from 1.7 to 1.9 $\mu g\,m^{-3}$ in BCN, LUG and NK. Thus, despite differences in percentages of diesel vehicles between sites, BC levels are almost equal. This fact may be explained by differences in meteorology and by considering the importance of biomass burning emissions in Lugano and coal fired power plants around London, which contribute to increase BC outputs (Szidat et al., 2007; Bigi and Harrison, 2010). Levels of BC were very high in MR, with an annual average of 7.8 $\mu g\,m^{-3}$ and decrease down to 3.5 $\mu g\,m^{-3}$ in Bern, accordingly with the lower vehicle flow. On the other hand, HU (0.7 $\mu g\,m^{-3}$) and SCO (0.8 $\mu g\,m^{-3}$) recorded the lowest concentrations of BC owing to a lesser impact of traffic in these smaller cities and favourable dispersive conditions (SCO). It is important to note that the ratio PM_{10}/BC is higher at urban background sites (9–18) than at traffic sites (4–8) due to the relative prevalence of secondary compounds. Maximum values of this ratio are observed in HU and SCO (26–33) as a consequence of the important contributions of dust, and also sea salt in SCO.

As regards N, 2009 averages ranged from 12 000–18 000 cm^{-3}, including the industrial site (with the highest levels), with this range increasing to 22 000–28 000 cm^{-3} at traffic sites due to the direct impact of primary exhaust emissions. N/BC ratios range from 6 to 6×106 particles ng^{-1} BC, with the exception of MR (2.8×106 particles ng^{-1} BC), HU (25×106 particles ng^{-1} BC) and SCO (15×106 particles ng^{-1} BC). The reasons behind these unusually low and high N/BC ratios will be discussed in the following sections.

Table 3. Data from the air quality instrumentation working during the sampling period.

	BARCELONA	LUGANO	NORTH KENSINGTON	BERN	MARYLEBONE	HUELVA	STA. CRUZ DE TENERIFE
PM_{10} ($\mu g\,m^{-3}$)	PM optical counters Grimm labortechnik GmB & Co. models 1107 and 1108	Reference equivalent beta measures	Reference equivalent TEOM-FDMS measures	Reference equivalent beta measures	Reference equivalent TEOM-FDMS measures	PM beta attenuation monitor (FAG FH-62)	PM optical counters Grimmlabortechnik GmB & Co
Black Carbon ($\mu g\,m^{-3}$)	Multi-angle absorption photometer (MAAP Thermo ESM Andersen Instrument) with PM_{10} inlet	Multi-angle absorption photometer (MAAP Thermo ESM Andersen Instrument) with PM_1 inlet	Magee AE-21 Aethalometer	Multi-angle absorption photometer (MAAP Thermo ESM Andersen Instrument) with PM_1 inlet	Magee AE-21 Aethalometer	Multi-angle absorption photometer (MAAP Thermo ESM Andersen Instrument) with PM_{10} inlet	Multi-angle absorption photometer (MAAP Thermo ESM Andersen Instrument) with PM_1 inlet
Number of particles ($n\,cm^{-3}$)	WCPC TSI model 3785 (N_{5-1000})	CPC TSI model 3022A (N_{7-1000})	CPC TSI model 3022A (N_{7-1000})	CPC TSI model 3022A (N_{7-1000})	CPC TSI model 3022A (N_{7-1000})	CPC TSI model 3776 ($N_{2.5-10000}$)	CPC TSI model 3776 ($N_{2.5-10000}$)
SO_2 ($\mu g\,m^{-3}$)	UV fluorescence	UV fluorescence	UV fluorescence		UV fluorescence	UV fluorescence	UV fluorescence
NO, NO_2, NO_x ($\mu g\,m^{-3}$)	Chemiluminescence	Chemiluminescence	Chemiluminescence	Chemiluminescence	Chemiluminescence	Chemiluminescence	Chemiluminescence
CO ($\mu g\,m^{-3}$)	IR absorption	IR absorption	IR absorption	IR absorption	IR absorption		IR absorption
O_3 ($mg\,m^{-3}$)	UV absorption	UV absorption	UV absorption	UV absorption	UV absorption	UV absorption	UV absorption

Table 4. Average values of the main parameters measured in each site under study: (a) average, maximum and minimum concentrations of atmospheric pollutants (b) vehicle fleet information and ratios of atmospheric pollutants in the units derived from those in (a). Maximum values between stations are in bold.

(a)	Barcelona Urban Background				Lugano Urban Background				North Kensington Urban Background			
	Average	St. Dev	Max	Min	Average	St. Dev	Max	Min	Average	St. Dev	Max	Min
PM_{10} ($\mu g\,m^{-3}$)	30	7	60	12	23	7	40	12	18	6	30	7
Black Carbon ($\mu g\,m^{-3}$)	1.7	0.6	3.8	0.7	1.8	0.9	3.6	0.6	1.9	0.7	3.4	0.8
Number of particles ($n\,cm^{-3}$)	16 847	5117	29 449	6140	14 945	9750	47 562	2751	12 134	5810	27 295	792
SO_2 ($\mu g\,m^{-3}$)	3.2	1.3	8.0	1.1	1.6	1.4	7.3	0.2	2.7	1.2	7.6	0.7
NO_x ($\mu g\,m^{-3}$)	58	27	163	17	25	18	80	4.4	46	22	112	13
NO ($\mu g\,m^{-3}$)	16	17	97	2	8	10	47	0.4	14	11	56	1.2
NO_2 ($\mu g\,m^{-3}$)	42	12	72	15	16	8	40	4	36	17	83	10
CO ($mg\,m^{-3}$)	0.4	0.1	0.8	0.2	0.3	0.2	0.8	0.1	0.3	0.1	0.5	0.2
O_3 ($\mu g\,m^{-3}$)	49	25	76	15	26	17	70	2	36	17	83	10

	Bern Road Site				Marylebone Road Site			
	Average	St. Dev	Max	Min	Average	St. Dev	Max	Min
PM_{10} ($\mu g\,m^{-3}$)	27	9	57	11	**32**	7	51	16
Black Carbon ($\mu g\,m^{-3}$)	3.5	1.3	7.1	1.3	**7.8**	2.7	14	2.5
Number of particles ($n\,cm^{-3}$)	**28 032**	13 650	93 078	8888	22 156	12 910	58 017	4753
SO_2 ($\mu g\,m^{-3}$)	–	–	–	–	6.7	2.7	13	1.6
NO_x ($\mu g\,m^{-3}$)	54	25	128	14	**233**	78	439	86
NO ($\mu g\,m^{-3}$)	27	19	89	5	**106**	27	178	49
NO_2 ($\mu g\,m^{-3}$)	24	7	42	10	**127**	53	261	29
CO ($mg\,m^{-3}$)	0.5	0.1	0.9	0.2	**0.7**	1.0	1.4	0.3
O_3 ($\mu g\,m^{-3}$)	17	11	43	3	13	7	34	5

	Huelva Urban Industrial				Sta Cruz Tenerife Urban Shipping			
	Average	St. Dev	Max	Min	Average	St. Dev	Max	Min
PM_{10} ($\mu g\,m^{-3}$)	23	9	58	6	21	7	34	7
Black Carbon ($\mu g\,m^{-3}$)	0.7	0.4	2.3	0.1	0.8	0.4	2.6	0.1
Number of particles ($n\,cm^{-3}$)	17 918	13 929	67 949	1091	12 008	7002	26 294	1076
SO_2 ($\mu g\,m^{-3}$)	**9**	5	27	3.1	4	3	15	0.4
NO_x ($\mu g\,m^{-3}$)	32	20	136	4.3	13	7	39	0.2
NO ($\mu g\,m^{-3}$)	7	5	30	0.4	7	4	21	0.1
NO_2 ($\mu g\,m^{-3}$)	23	16	94	4.1	7	4	18	0.1
CO ($mg\,m^{-3}$)	–	–	–	–	0.2	0.04	0.3	0.02
O_3 ($\mu g\,m^{-3}$)	**61**	22	107	24	27	7	79	11

Table 4. Continued.

(b)	BCN	LUG	NK	Bern	MR	HU	SCO
Vehicles km^{-2}	**6100**	1400	1500	1600	1500	620	1100
NO_2/BC	24.6	9.0	19.2	6.9	16.3	**32.1**	9.0
NO/BC	9.2	4.6	7.2	7.8	**13.6**	10.1	9.1
NO_x/BC	34	14	24	16	30	**45**	17
CO/BC	0.2	0.2	0.2	0.1	0.1	–	0.2
NO_2/NO	2.7	2.0	2.7	0.9	1.2	**3.2**	1.0
PM_{10}/BC	18	13	9	8	4	**33**	26
N/BC	9910	8303	6386	8009	2840	**25 598**	15 010
N/SO_2	5265	**9341**	4494	–	3307	1948	3431
NO_2/NO_x	0.7	0.7	**0.8**	0.4	0.5	0.7	0.5
NO_x/CO	144	82	153	109	333	–	88

Concerning gaseous pollutants, SO_2 levels reach between 1.8 µg m^{-3} (LUG) and 3.5 µg m^{-3} (SCO) in the urban background stations. The slightly higher levels measured at BCN and SCO are caused by the significant influence of shipping emissions. Maxima SO_2 levels were recorded at the traffic site of MR (6.7 µg m^{-3}), as a direct effect of exhaust emissions (according to data from the UK National Atmospheric Emission Inventory, the emission factor of SO_2 from road vehicle engines is 11.5 Kilotonne Mt^{-1} fuel consumed) and at HU (9.2µg m^{-3}), due to the emissions from a large copper smelter, fertilizer and oil refinery industries.

NO concentrations reach 7–16 µg m^{-3} at urban background sites and 27–106 µg m^{-3} at the traffic ones. The lowest values were registered for LUG, HU and SCO. The same trends were observed for CO concentrations, which ranged from 0.2 to 0.4 mg m^{-3} at urban background sites and from 0.5 to 0.7 mg m^{-3} at traffic locations, as this gaseous pollutant reflects proximity and intensity of the traffic flow. The NO/BC ratio ranges from 7 to 10 in most of the sites, with the exception of LUG (5), probably due to a higher influence of biomass burning, increasing BC but not proportionally NO levels, and MR (14), as a result of the proximity to fresh road traffic emissions. The influenced of biomass burning in Lugano is also indicated by the diurnal cycle of CO and PM concentrations, with a more pronounced peak in the evening than the one obtained for NO_x levels. Similar results have been reported in previous studies in nearby regions (Sandradewi et al., 2008).

On the other hand, the variability of CO/BC ratio does not reflect the composition of the vehicle fleet in each city. Maximum values are recorded for BCN (235), while minimum values are obtained in MR (90). In LUG, NK, Bern and SCO values ranged between 143 and 188.

NO_2 levels reached 16–42 µg m^{-3} at the urban background environments, with higher concentrations in BCN, probably related to the higher percentage of diesel vehicles (with enhanced primary NO_2 and NO_x emissions) in fleet, higher O_3 levels (leads to faster NO oxidation to NO_2) and the very elevated car density (6100 cars km^{-2}). At the traffic sites, NO_2 concentrations ranged from 24–127 µg m^{-3}, with the highest levels being recorded at MR, with the highest traffic flow (80 000 vehicles day^{-1}) and probably also to a significant proportion of diesel in the vehicle fleet of London (Carslaw et al., 2005). In fact, the ratio NO_x/CO increases with the proportion of diesel vehicles and is very similar in BCN and NK. In SCO, NO_2 concentrations reach relatively low levels (7 µg m^{-3}) due to the good ventilation conditions on the island, NO_2 levels mostly represent the primary emissions.

Marked differences in the NO_2/NO ratio are only found between traffic (0.9–1.2) and urban background sites (2–3). These values are in the order of those obtained in other sites in Europe (Chaloulakou et al., 2007) and seem to be independent of the percentage of diesel vehicle in the fleet. Thus, despite certain evidences described above, differences in pattern emissions of gasoline and diesel vehicles are not clearly shown in the stations under study. It should be noted that NO_2 measurements can be overestimated because of interferences of oxidized nitrogen compounds in the conventional instruments equipped with molybdenum converters (Steinbacher et al., 2007).

Finally, O_3 concentrations range between 26 and 49 µg m^{-3} at urban background stations, including on the island. Very high values are measured at BCN, as a result of an intense photochemical activity. At traffic sites, values are about 13–16 µg m^{-3} as a consequence of a major consumption of O_3 by NO. Levels at HU were the highest (61 µg m^{-3}) as a direct consequence of high industrial emissions and solar radiation intensity.

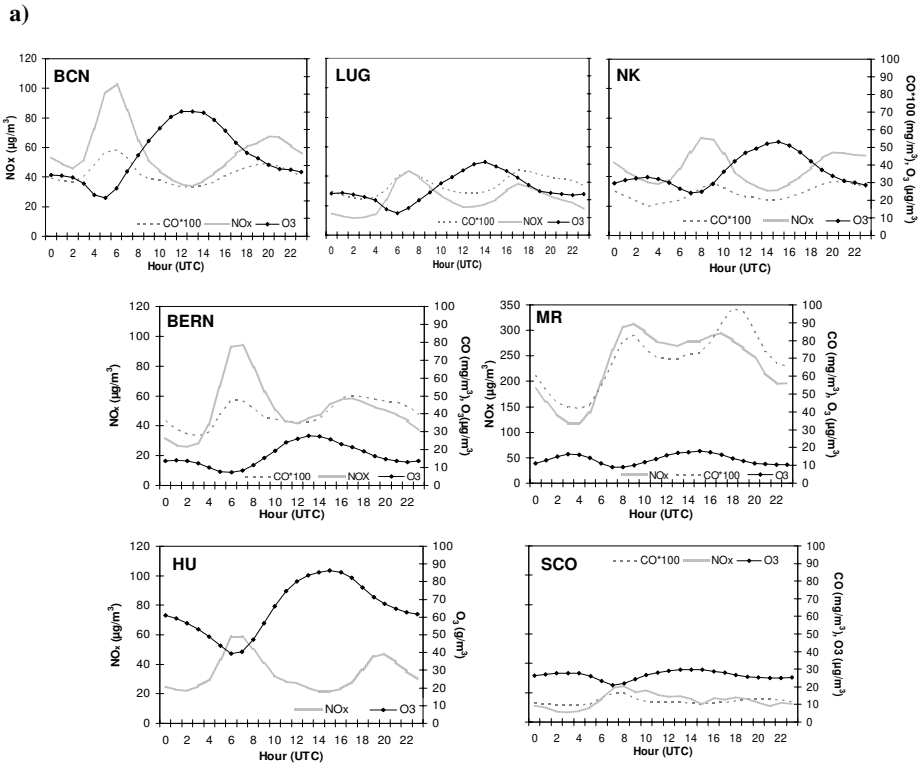

Fig. 2a. Daily cycle of: gaseous pollutants concentrations (CO, NO_x and O_3) levels for each monitoring site.

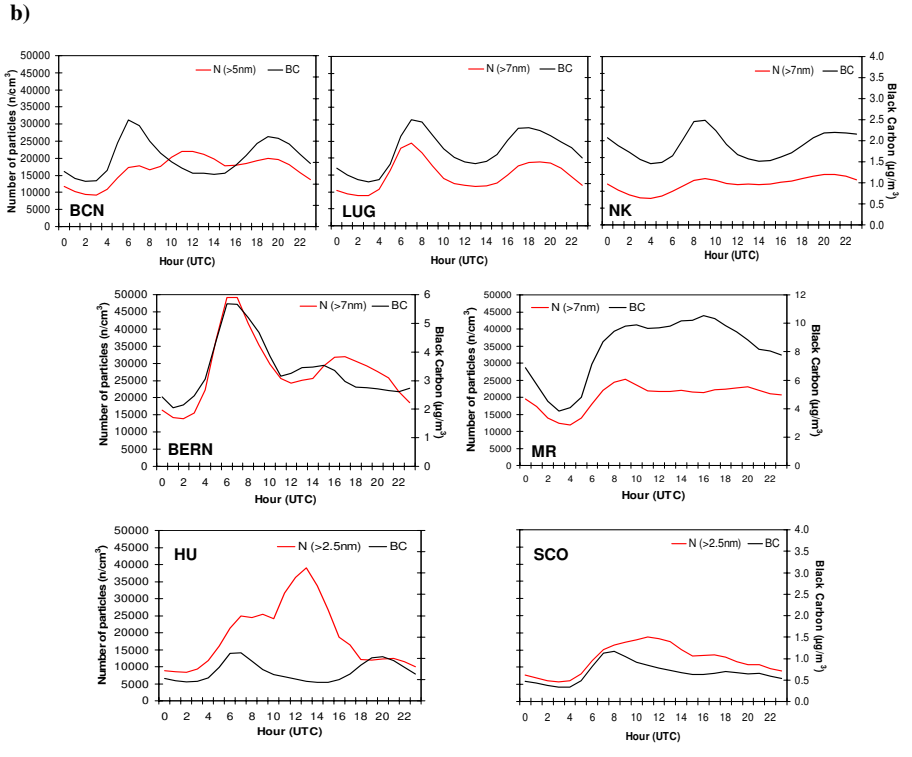

Fig. 2b. Daily cycle of: Black Carbon (BC) and Number concentration (N) levels for each monitoring site.

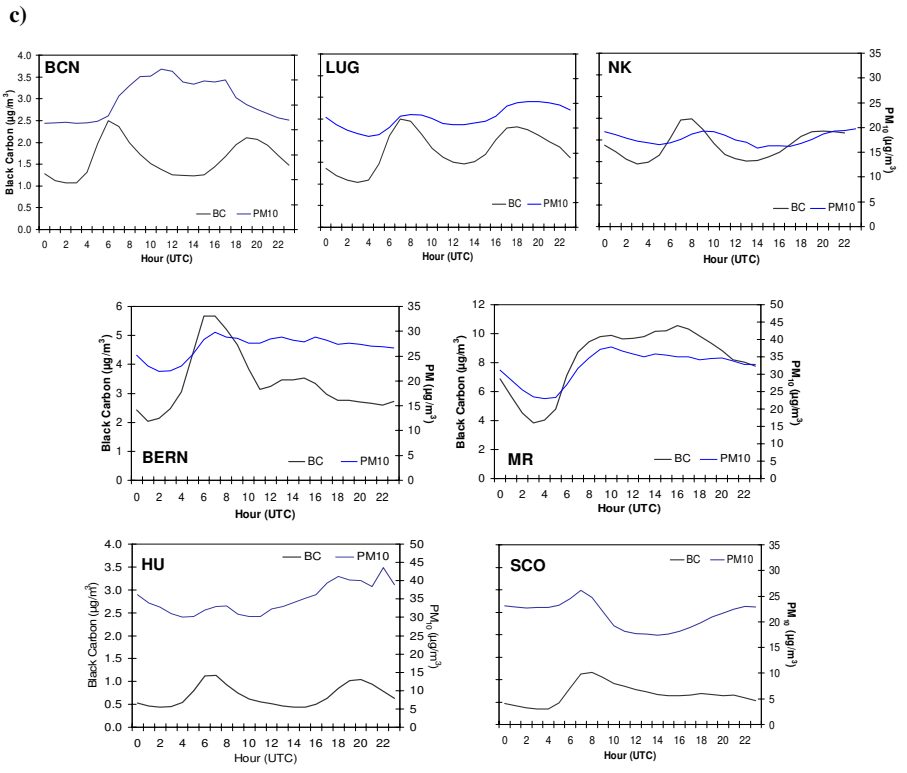

Fig. 2c. Daily cycle of: BC and PM_{10} levels for each monitoring site.

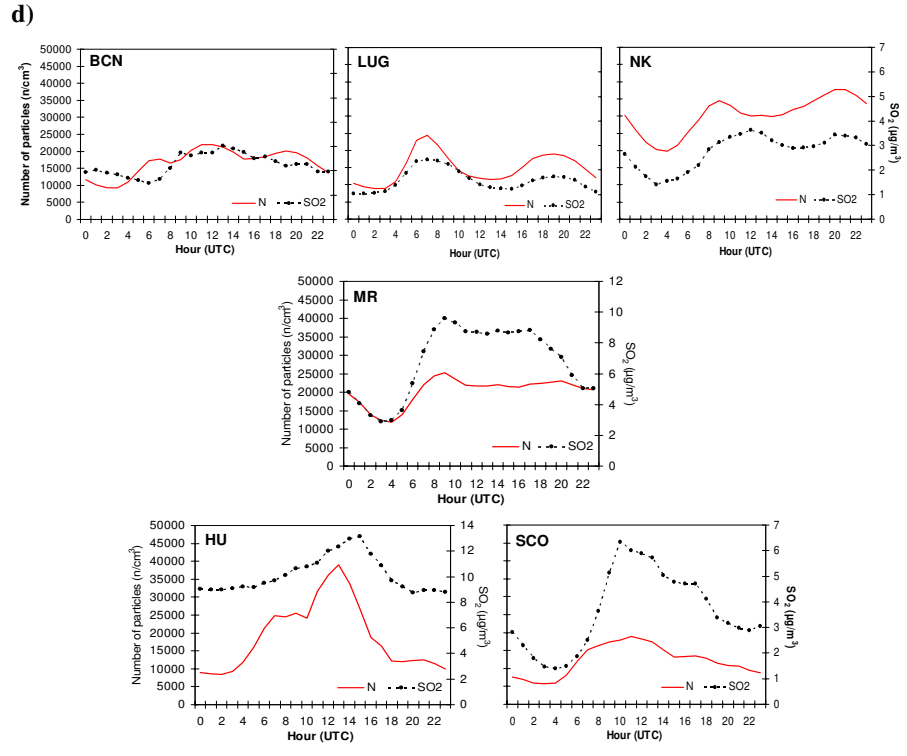

Fig. 2d. Daily cycle of: SO_2 levels for each monitoring site.

4.2 Temporal variability of atmospheric pollutants

Figure 2a shows the 2009 average daily cycle of gaseous pollutants for each site. For all sites levels of NO_x ($NO_2 + NO$) and CO follow the diurnal pattern of traffic intensity, reaching a maximum during the morning rush hour (07:00–09:00 UTC), decreasing during the day because of atmospheric dilution processes, and increasing again in the evening (17:00-20:00 UTC). An increment of the ratio CO/NO_x is observed comparing the evening peak with the one recorded at morning rush-hours. This phenomenon is more marked in BCN and Bern but the tendency is equal for all the stations. While CO emissions are a tracer of gasoline vehicles, NO_x reflects emissions from diesel vehicles, so a possible explanation of the tendency above is the major presence of delivery HDV and LDV and of school buses in the morning.

The evolution of O_3 levels shows a typical diurnal pattern, with an increase at midday coinciding with the maximum photochemistry and vertical dilution. At SCO O_3 daily patterns differ from the above trend, with levels at night similar to those registered at midday, a behaviour induced by the continuous supply of fresh oceanic air masses coupled with low local NO levels.

The same daily evolution described for NO_x and CO is followed by levels of BC (Fig. 2a and b), except in the case of Bern, where the second peak of BC is produced earlier than expected. The cause for the anomalous hourly trend detected in Bern is still unclear, although it is possibly related to the fact that the BC and the gaseous pollutant monitors were not co-located, but instead were distant by approximately 150 m on opposite sides of the road. The BC monitor was located closer to road traffic and to a railway. In all the other monitoring stations, BC levels traced accurately the impact of vehicle exhaust emissions on air quality, increasing with the proximity to roads, the density of vehicles, and the traffic flow. One may think that there is no need to measure BC levels if this aerosol component follows the variability of CO, NO and NO_2, however, differences among sites in the ratios CO/BC (ranging from 90–235) and NO_2/BC (ranging from 7–32) indicate that BC should be measured.

The combination of PM_{10} and BC in urban areas potentially constitutes a useful approach for air quality monitoring (Fig. 2c). While BC daily cycle is mostly determined by vehicle exhaust emissions, PM_{10} concentrations at these sites are also governed by non-exhaust particulate emissions resuspended by traffic, by midday atmospheric dilution and by other non-traffic emissions (see LUG and NK patterns in Fig. 2c). PM_{10} levels at the traffic sites remained nearly constant from the morning until the evening peak due to the effects of resuspension processes. In the case of BCN, concentrations increase at midday when sea breezes transport the re-suspended mineral material from the city towards the monitoring site. Similar results were reported in earlier studies (Querol et al., 1998; Harrison et al., 2001; Querol et al., 2001, 2005; Charron and Harrison, 2005). In contrast, PM_{10} concentrations in HU reach the highest values at night due to the seaward transport of aged particulate pollutants. During daylight, winds blow inland from the Atlantic Ocean carrying emission plumes with gaseous pollutants from industrial estates (Sánchez de la Campa et al., 2007), accounting for the different daily cycle of PM and gaseous pollutants.

N is also an appropriate tracer of traffic emissions in certain environments, but it has been reported to be highly influenced by photochemically induced nucleation (Pey et al., 2008; Pérez et al., 2010; Fernández-Camacho et al, 2010; Cheung et al., 2010). Peaks of N and BC at morning and afternoon rush-hours (07:00–09:00 and 17:00-20:00 UTC) are coincident in all the stations studied, with N being mainly influenced by primary aerosols and by the formation of new particles during the dilution and cooling of the vehicle exhaust emissions (Mariq et al., 2007, Wehner et al., 2009). Furthermore, at BCN, HU and SCO, N shows a second peak at midday, simultaneously occurring with the BC decrease, confirming that this peak could not be a consequence of primary emissions from road traffic, but of secondary formation of particles by means of photochemical nucleation processes from gaseous precursors. This midday nucleation takes place as a consequence of the high solar radiation, the growth of the mixing layer, the increase in wind speed and the consequent decrease of pollutants concentrations. This phenomenon is not observed in the selected northern and central European cities, where the decrease of N at midday was in the order of that of BC. The occurrence of nucleation events at midday in BCN was supported by means of an SMPS (scanning mobility particle sizers) working during the international DAURE campaign in 2009 (http://cires.colorado.edu/jimenez-group/wiki/index.php/DAURE) when it was observed that the increment of N at midday was caused by a marked increment of nucleation mode particles (N_{5-20}) (Fig. S4). Because of the similar pattern of N and meteorological parameters (global radiation, wind speed, wind direction and boundary layer), it was estimated that results regarding nucleation episodes from Barcelona could be extrapolated to these sites in south-Europe.

In the case of traffic sites, daily patterns of BC and N follow an opposite trend since 11:00 UTC, so that the peaks of N in the evening show slight delays. The opposed trends of BC and N are specially significant in Bern, where the second peak of BC is registered earlier than in the rest of stations and is about 40 % lower than morning peak. This lack of parallelism between N and BC is due to a source of N other than traffic, which may be interpreted as secondary particles formed in the evening, when lower temperatures and lower mixing heights occur. The different location of the instrumentation can also be responsible for the dissimilarities. Sulphuric acid has been identified as a key nucleating substance in the atmosphere (Curtis et al., 2006) as atmospheric OH concentrations correlate well with UV solar radiation (Rohrer and Berresheim, 2006). Because UV

radiation has not been measured continuously at most of the stations, we use the global intensity of solar radiation (SR) as its proxy with the purpose of obtaining the product of solar radiation ($W\,m^{-2}$), SO_2 ($\mu g\,m^{-3}$), O_3($\mu g\,m^{-3}$) and H_2Ov ($g\,Kg^{-1}$). This product was used as a surrogate parameter for H_2SO_4 production. Mean values of the product at midday (11:00-14:00 UTC) were 171 $W\mu g^2\,m^{-8}$ in NK, 160 in MR, 107 in LUG, 1103 in BCN, 5271 in HU and 1259 in SCO, confirming the potential for secondary formation of particles at midday in the southern European cities under study.

Daily trends of SO_2 levels in BCN, HU and SCO suggest a significant source of this pollutant different from vehicle exhaust emissions (Fig. 2d). SO_2 levels in BCN attain a maximum from 9:00 to 13:00 UTC and around 10:00 UTC in SCO. At this time, breezes drive harbour emissions across the city, and thus in these cases this pollutant may be attributed to shipping emissions. In HU, the northward inland breeze blowing during the afternoon favours the inland transport of the SO_2 plumes over the city and the mixing of urban and industrial pollutants (Fernández-Camacho et al., 2010). In LUG and MR, SO_2 concentrations are directly dependent upon exhaust emissions, reaching higher values with increases in traffic volume. In NK the diurnal cycle is also highly influenced by traffic, but maximum levels are registered at midday due probably to the convective mixing of upper tropospheric layers, polluted with SO_2 from power plants (Bigi and Harrison, 2010).

On a weekly scale, the study of the daily evolution of N and BC for each day of the week and each station (Fig. 3) shows that the daily evolution was not the same at weekends because the morning road traffic maximum disappears, and a relatively smoother daily evolution in aerosol concentrations during daylight was observed. Lower PM, N and BC levels at weekends are responsible for the sharper peak of N at midday registered for BCN, HU and SCO (especially marked on Sundays) due to the favourable conditions (low atmospheric pollution) for secondary aerosol formation by nucleation processes to take place. Low pollutant concentrations hinder condensation and coagulation processes but favour nucleation activated by photochemistry.

Furthermore, a seasonal trend for BC and N levels is not detected in stations with a direct influence of traffic (Fig. 4), with levels remaining relatively steady during the whole year. However, at LUG, NK and HU, concentrations are much lower in summer, coinciding with the higher dispersive conditions. By contrast, SCO accounts for the maximum values in summer probably due to major maritime traffic intensity. As expected, the N peaks at midday registered in BCN, HU and SCO, compared with the hourly average, are higher in summer.

CO and NO_x concentrations follow the same seasonal trend described above for BC and N (Fig. S1). However, NO_x declines in summer are also evident in BCN. As expected, O_3 levels present an opposite tendency, increasing

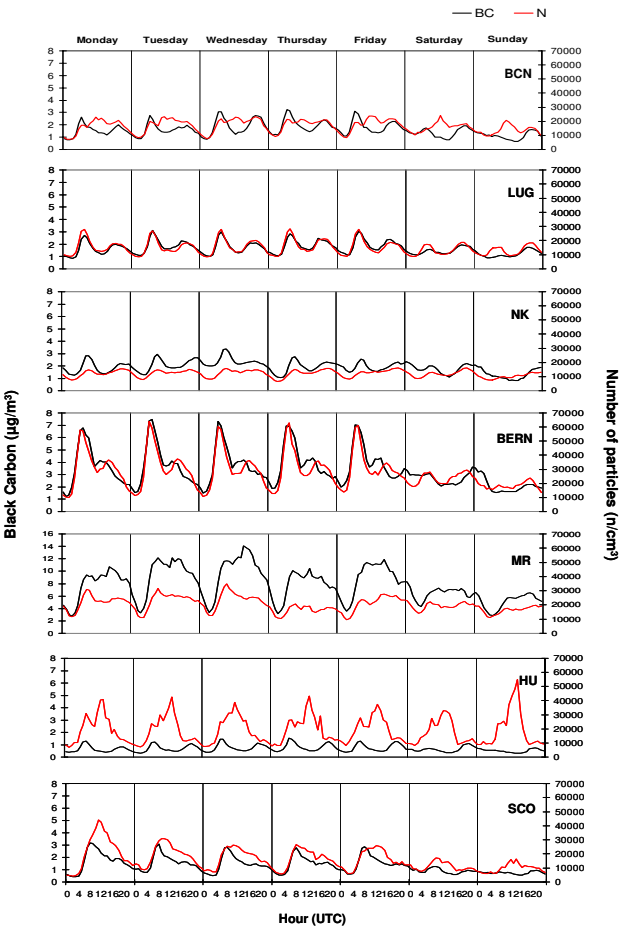

Fig. 3. Daily cycle of: BC and N for each day of the week.

during the months with the highest solar radiation intensities (Fig. S2). In BCN and HU, those periods with maximum concentrations of O_3 match with those of maximum concentrations of N at midday. This fact highlights the direct dependence of O_3 and N on photochemistry.

At SCO, O_3 levels are associated with processes of long-range transport and they show the typical spring maximum of the subtropical latitudes (Oltmans and Levy, 1994).

4.3 BC/N relationship: similarities and differences across Europe

Parallelisms between BC and N are repeatedly observed in urban environments owing to the impact of vehicle exhaust emissions (Zhu et al., 2002; Fruin et al., 2004; Rodríguez and Cuevas, 2007; Pérez et al., 2010). The degree of correlation of these two parameters has been studied for each site using the methodology described by Rodriguez and Cuevas (2007). Different behaviours were observed depending on the time of the day.

BC vs. N scatter plots were analysed for four different periods of the day (Fig. S3), specifically: 07:00–09:00,

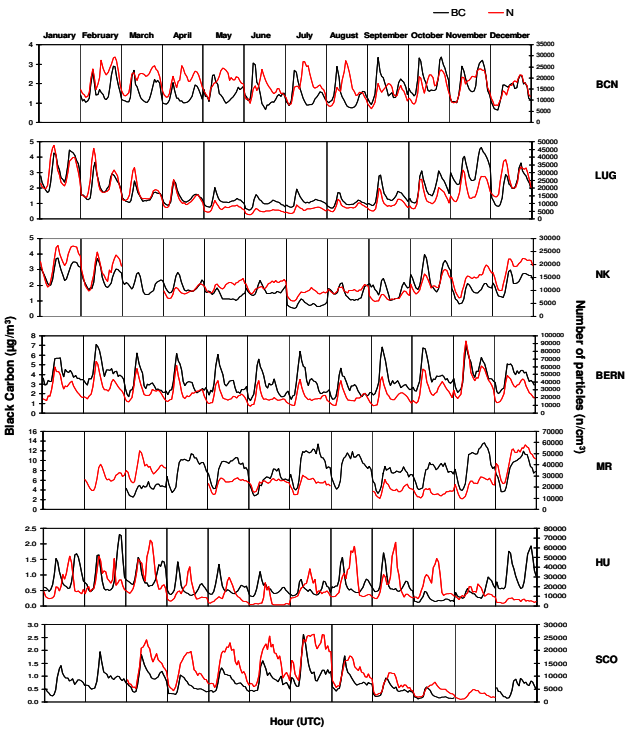

Fig. 4. Daily cycle of: BC and N for each month.

11:00–14:00, 18:00–21:00, 01:00–03:00 UTC. The selection of these time ranges is determined by variations in pollutant levels, mainly governed by emission patterns and atmospheric dynamics. The first period stands for the traffic rush-hours, accounting for the highest exhaust emissions. At 11:00–14:00 UTC there is an increase in the height of the mixing layer and the highest solar radiation intensity is reached, with the consequent development of mountain and sea breezes. These factors result in a dilution of atmospheric pollutants. The 18:00–21:00 UTC period represents the evening traffic rush hours, with pollutant concentrations in the order of those registered in the morning rush-hours, this period is also characterized by the influence of biomass burning emissions during winter, specially significant at north and central European locations. Finally, the night period is characterized by the lowest traffic intensity; however, the decrease of the height of the mixing layer causes a concentration of pollutants.

At any time and for all the stations, the N versus BC scatter plots are grouped between two defined lines with slopes S1 and S2 representing the minimum and maximum N/BC ratios, respectively (Fig. S3). S1 is interpreted as the minimum number of primary particles arising from vehicle exhaust emissions per each nanogram of ambient air BC. The observed increases in N/BC ratios up to reach the maximum S2 value are caused by means of enhancements in the new particle formation rates during the dilution and cooling of the vehicle exhaust emissions and/or in ambient air.

This analysis of the relationship between BC and N is performed assuming that BC in urban areas is an accurate tracer of primary traffic emissions. A similar approach was used by Turpin and Huntzicker (1995) to differentiate primary and secondary organic carbon

Important differences in S1 are observed between sites at 11:00–14:00 UTC (Table 5). It is important to note that dissimilarities are partly caused by the selection of CPC model at each location, since higher the cut size of the instrument is, lower the N/BC ratio will be. S1 ranges 3.1–4.1×106 particles ng^{-1} BC in central and north European cities, with the lowest values registered at the traffic sites. The ratio, expressed in 10^6 particles ng^{-1} BC, increases to 6.5 in BCN, 15.6 in SCO and 28.4 in HU. South European cities recorded the highest solar radiation just occurring when the atmospheric dynamics result in the highest dilution of pollutants (midday). This dilution is enhanced by the development of sea breezes in coastal cities. The combination of these factors sets a favourable scenario for nucleation events to occur. The formation of secondary particles by nucleation might account for the marked increase of S1 from 07:00–09:00 UTC to 11:00–14:00 UTC in BCN, HU and SCO. Furthermore, the influence of shipping emissions in these cities, together with an important industrial source in HU, adds the presence of gaseous precursors (mainly SO_2) to the conditions that favour nucleation.

As expected, S1 at 18:00–21:00 UTC is in the order of those ratios at 07:00–09:00 UTC (5.7×10^6 particles ng^{-1} BC in BCN, 8.7×10^6 particles ng^{-1} in HU, 11.1×10^6 particles ng^{-1} BC in SCO and 3.1–5.3×106 particles ng^{-1} BC in the rest of stations), although values are slightly higher at 18–21 h at most of the sites, probably due to a major gas to particle transfer of matter by condensation and/or nucleation. In MR, the N/BC ratios measured at 7–9 h and at 18:00–21:00 h are very similar, highlighting the lower relevance of secondary aerosol at this site, with persistently high exhaust emissions.

At night (01:00–03:00 UTC), the ratio ranges between 3.4–4.7 10^6 particles ng^{-1} BC for most of the sites, increasing to 8.3 10^6 particles ng^{-1} BC in HU and 9.2 10^6 particles ng^{-1} BC in SCO. In spite of the traffic intensity reduction, the decrease of the height of the mixing layer promotes condensation processes, resulting in similar N/BC ratios as those calculated at traffic rush-hours.

Figure 5 shows the correlations between the mean annual hourly levels of N and BC for the above S1 ratios (Table 5) during the periods 07:00–09:00, 11:00–14:00, 18:00–21:00 and 01:00–03:00 UTC for the different sites. It is evident that diurnal (07:00–09:00 and 11:00-14:00) N-BC patterns for southern Europe differ markedly from the general correlation found for central Europe, with higher N/BC trend. Thus, during these diurnal periods the cities from central Europe and UK are aligned along a very well fitted regression line between BC and N. The position of these cities (black and blue symbols) along the line is dependent on the traffic flow

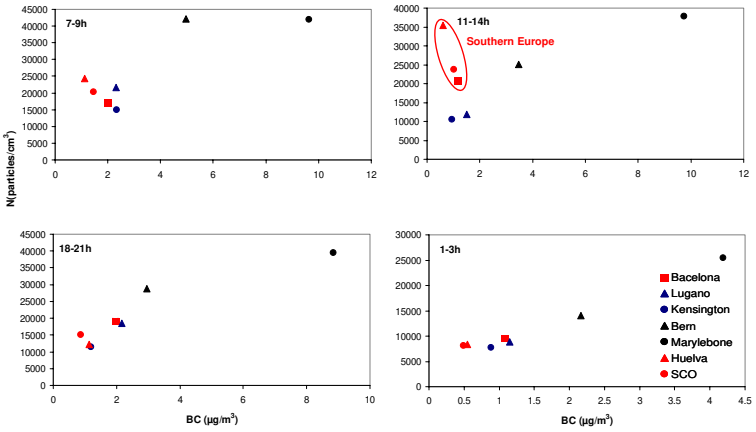

Fig. 5. Correlation between: **(a)** the mean annual hourly levels of N and BC for the periods 07:00–09:00, 11:00–14:00, 18:00–21:00 and 01:00–03:00 (UTC) for the different study sites.

Table 5. Values of S1 and S2 representing the minimum and maximum N/BC ratios for each site.

	$N(n\,cm^{-3})/BC(ng\,m^{-3})$							
	S1				S2			
	07:00–09:00 h	11:00–14:00 h	18:00–21:00 h	01:00–03:00 h	07:00–09:00 h	11:00–14:00 h	18:00–21:00 h	01:00–03:00 h
BCN	5.1	8.5	5.7	4.7	24.5	104.5	20.1	10.4
LUG	3.1	4.1	4.7	3.4	20.9	10.5	22.3	44.5
NK	3.6	3.9	4.6	4.4	14.9	18.6	14.7	18.7
Bern	3.6	3.1	5.3	3.5	18.9	13.9	23.2	17.0
MR	2.9	3.2	3.1	3.9	6.3	8.7	5.1	6.1
HU	8.7	28.4	8.7	8.3	54.2	226.4	35.9	56.4
SCO	9.9	15.6	11.1	9.2	22.1	71.3	19.8	41.5

and proximity to roads as well as meteorological dispersion, with a clear positive slope. However, the southern European cities (red symbols) are well off this regression line. During some periods there seems to even be a negative slope. During the nocturnal periods both northern-central and southern European cities seem to fit the same regression line with a positive slope.

As regards S2, the observed trends are almost the same as those described for S1. However, the enhancement of N/BC at midday in BCN, HU and SCO is more marked when considering S2. In Bern, an increase of S2 is produced in the afternoon (18:00–21:00 UTC), since the peak of BC is produced earlier than expected. Such is the case of LUG, where the maximum ratio at 18:00–21:00 and mainly at 01:00–03:00 UTC is higher than in the rest of central and north European sites. This could be attributed to the influence of biomass burning emissions, since volatile organic compounds (VOCs) from residential wood combustion may lead to significant secondary non-fossil organic aerosols in winter as suggested to be important in Zürich (Lanz et al., 2008) and in Roveredo (Lanz et al., 2010).

Similar ratios have been reported in previous studies in Milano (Rodriguez and Cuevas, 2007), where the new particle formation contributions result in a strong correlation between the diurnal cycle of N/BC ratio and the solar radiation intensity.

The results indicate that BC is an appropriate tracer for the intensity and proximity of traffic emissions, and as a suitable indicator of the dynamics of the atmospheric mixing layer. In central and north European cities, N daily trends are similar to those of BC, whereas in south Europe, N is highly influenced by the occurrence of nucleation processes induced by photochemistry at midday.

4.4 Differences in primary emissions and nucleation enhancements across European cities

In order to quantify the sources and processes contributing to UFP, particle number concentration data were analysed using the methodology described by Rodríguez and Cuevas (2007), where:

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

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

with N being the total number concentration; N1 the minimum primary emission of vehicle exhaust; N2 accounting

for: (a) secondary particles formed in the atmosphere by homogeneous nucleation or other heterogeneous reactions from gaseous precursors arising from traffic or any urban source, (b) primary particles from other sources different to traffic such as biomass burning, resuspension, residential emissions and biogenic emissions, and (c) inherited particles present in the air mass, which receives anthropogenic emissions in a given point in time; BC representing the Black Carbon concentrations; and S1 the minimum N vs. BC slope observed during the morning rush hours (07:00–09:00 UTC). Values of S1 (expressed as 10^6 particles/ngBC) of 3.2 at LUG, 3.6 at NK and Bern, 2.9 at MR, 5.1 at BCN, 8.7 in HU and 9.9 in SCO were used. These differences in the S1 values are caused by: 1) the use of different CPC models (with different cut sizes) at different sites (the lowest S1 values are observed at the sites where the CPC with the largest cut size, 7 nm, was used) and (2) the influence of the ambient air conditions on the new particle formation during dilution and cooling of the vehicle exhaust.

Figure 6 shows hourly average values of N1 and N2 for every day of the week. Differences between sites are marked, observing two different patterns: stations with parallel cycles of N1 and N2 at midday (LUG and Bern) and stations with a clear decoupling of the two components, indicating no dependence on exhaust emissions of N2 at midday (BCN, HU, SCO, NK and MR). It is a consequence of the described nucleation processes favoured by photochemistry.

Nonetheless, an increase of N2 not coinciding with N1 is also observed in NK possibly related with the midday SO_2 increase from power plants, around two hours before (12:00 UTC) as a result of the downward mixing upper tropospheric layers (Fig. 2d). This association between increases of N and power plant emissions has been observed in previous studies (Brock et al., 2002).

Table 6 lists the total average percentages of N1 and N2 and the average percentage at midday (11:00-14:00 UTC) on an hourly basis for each station. N1 (minimum primary emission of vehicle exhaust) accounts for 46, 38 and 46 % of the total N during the whole sampling period in BCN, HU and SCO, respectively. These percentages are quite similar to the one registered in LUG in winter (38 %), significantly lower than the percentage obtained in summer (53 %), maybe as a direct consequence of SOA formation from biomass burning emissions. The value increases to 54 % in NK, 45 % in Bern and to 78 % in MR, as a consequence of the important and consistent traffic impact. In south European cities, a 64 to 85 % N2 contribution is observed at midday (11:00–14:00 h UTC, representing secondary parts from gaseous precursors, primary parts from non-traffic sources, and/or particles inherited in the air mass). As previously reported this high N2 load is caused by the combination of 3 processes: (1) increased solar radiation, (2) the dilution of pollutants in an increased boundary layer height, and (3) the input of SO_2 from a source different than traffic exhaust emissions. These high N2 loads are also obtained in the same cities on

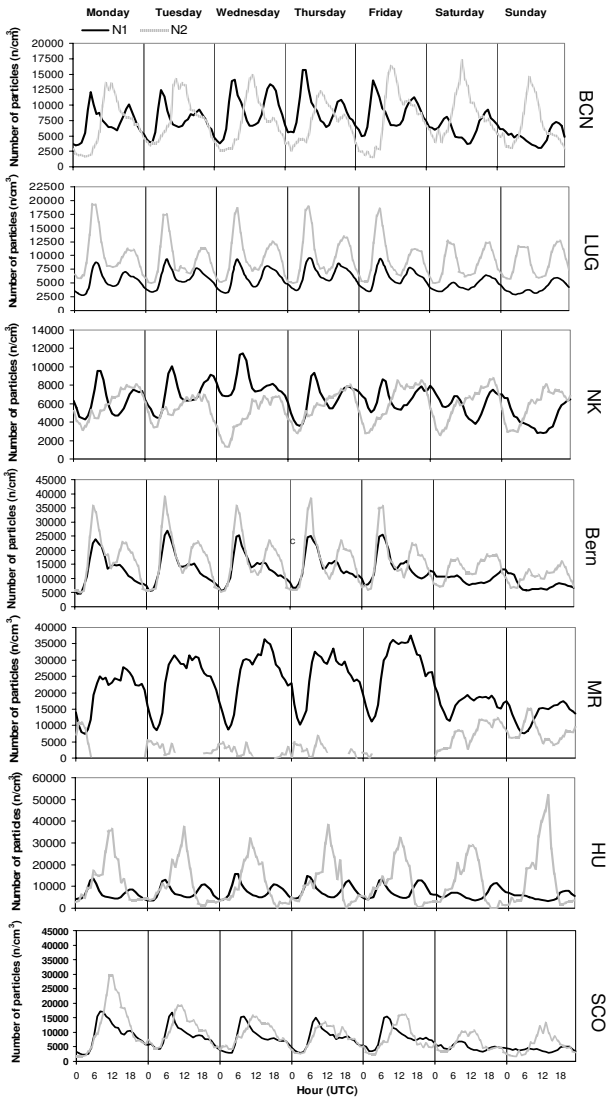

Fig. 6. Daily cycle of: N1 and N2 for each day of the week

a mean daily basis (66–80 %) during Sundays, mainly due to the lower levels of atmospheric pollutants.

Considering the relatively high concentrations of SO_2 at MR (with an average concentration at midday about 70 % higher than those registered in BCN and SCO) and the very high primary N load obtained, it can be stated that higher concentrations of SO_2 are not enough to achieve an enhancement of the secondary N load, but the combination with other factors such as solar radiation intensity and dilution (favouring decreases in PM levels) appears to be essential. This is supported by the observation of frequent nucleation events at the rural Harwell (UK) site with lower SO_2 concentrations (Charron et al., 2007).

To further confirm this hypothesis, Spearman rank correlation (ρ) tests were used to assess the relationship between N2 and different factors, specifically: N2 vs. SO_2*

Table 6. Total average percentages of N1 and N2 and average percentages at midday (11:00–14:00 h UTC) on an hourly basis.

%	BCN	LUG	NK	Bern	MR	HU	SCO
N1	46	39	54	45	78	38	47
N2	54	61	46	55	22	62	53
N1 (11:00–14:00 h UTC)	31	41	45	49	91	15	36
N2 (11:00–14:00 h UTC)	69	59	55	51	9	85	64

solar radiation intensity, N2 vs. wind velocity and N2 vs. wind direction on an hourly basis. Positive correlations between N2 and SO_2* solar global radiation were obtained in HU ($\rho = 0.86$), BCN ($\rho = 0.67$) and SCO ($\rho = 0.78$) with a level of significance of 0.01. The coefficient for the same test resulted lower than 0.20 in north and central European sites. No significant correlations were found in any case when analysing wind components. Nevertheless, it is known that enhancements in solar radiation intensity directly promote the development of sea breezes. This change in wind direction and velocity, coupled with increases in the mixing layer high, causes the dilution of atmospheric pollutants, favouring nucleation processes (Ketzel et al., 2004; Lee et al., 2008).

According to the results obtained it is clearly evidenced that N variability in different European urban environments is not equally influenced by the same emission sources and atmospheric processes.

5 Conclusions

This study shows the results of the interpretation of the 2009 variability of levels of PM, Black Carbon (BC), particle number concentration (N) and a number of gaseous pollutants at seven selected urban air quality monitoring sites covering road traffic, urban background, urban-industrial, and urban-shipping environments, from southern, central and northern Europe.

The results show that the variations of PM and N levels do not always reflect the variation of the impact of road traffic emissions on urban aerosols. However, BC levels vary proportionally to those of traffic related gaseous pollutants, such as CO, NO_2 and NO. Due to this high correlation, one may suppose that monitoring the levels of these gaseous pollutants would be enough to extrapolate exposure to BC levels. However the BC/CO, BC/NO_2 and BC/NO ratios vary widely among the studied cities, as a function of the distance to traffic emissions, the vehicle fleet composition and the influence of other emission sources such as biomass burning. Thus, BC is a relevant indicator for the impact of anthropogenic emissions at a measurement site and should therefore be measured in air quality monitoring networks. The combination of PM_{10} and BC in urban areas potentially constitutes a useful approach for air quality monitoring. Thus, BC is governed by vehicle exhaust emissions, while PM_{10} concentrations at these sites are also governed by non-exhaust particulate emissions resuspended by traffic, by midday atmospheric dilution and by other non-traffic emissions.

A subsequent question is focused on the evaluation of the variability of levels of N and the comparison with those of BC. The results indicate a narrow variation of primary road traffic N/BC ratios during traffic rush hours, while a wide variation of this ratio was determined for the noon period. Although in central and northern Europe N and BC levels tend to vary simultaneously, not only during the traffic rush hours but also during the whole day, in southern Europe maximum N levels coinciding with minimum BC levels are usually recorded at midday. These N maxima recorded in southern European urban background environments are attributed to midday nucleation episodes occurring when gaseous pollutants are diluted and maximum insolation and O_3 levels occur. The occurrence of SO_2 peaks may also contribute to the incidence of midday nucleation burst in specific industrial or shipping influenced areas, although at several central European sites similar levels of SO_2 are recorded without yielding nucleation episodes.

According to the results obtained it is clearly evidenced that N variability in different European urban environments is not equally influenced by the same emission sources and atmospheric processes. Therefore, we conclude that N variability does not always reflect the impact of road traffic on air quality in southern Europe, whereas BC is a more consistent tracer of such influence. However, N should be measured since ultrafine particles (<100 nm) may have large impacts on human health based on the very fine grain size that may reach the cardiovascular and cerebrovascular systems and the potential toxicity (Pérez et al., 2009).

Supplementary material related to this article is available online at: http://www.atmos-chem-phys.net/11/6207/2011/acp-11-6207-2011-supplement.pdf.

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References

Alonso-Pérez, S., Cuevas, E., Querol, X., Viana, M., and Guerra, J.C.: Impact of the Saharan dust outbreaks on the ambient levels of total suspended particles (TSP) in the marine boundary layer (MBL) of the Subtropical Eastern North Atlantic Ocean, Atmos. Environ., 41, 9468–9480, 2007.

Anderson, H. R., Bremner, S. A., Atkinson, R. W., Harrison, R. M., and Walters, S.: Particulate matter and daily mortality and hospital admissions in the west midlands conurbation of the United Kingdom: associations with fine and coarse particles, black smoke and sulphate, Occup. Environ. Med., 58, 504–510, 2001.

Baldasano, J. M., Plana, J., Gonçalves, M., Jiménez, P., Jorba, O., and López, E: Mejora de la calidad del aire por cambio de combustible a gas natural en automoción: Aplicación a Madrid y Barcelona, Fundación Gas Natural, Spain, 2007.

Bigi, A. and Harrison, R. M.: Analysis of the air pollution climate at a central urban background site, Atmos. Environ., 44, 2004–2010, 2010.

Boy, M. and Kulmala, M.: Nucleation events in the continental boundary layer: Influence of physical and meteorological parameters, Atmos. Chem. Phys., 2, 1–16, doi:10.5194/acp-2-1-2002, 2002.

Brock, C. A., Washenfelder, R. A., Trainer, M., Ryerson, T. B., Wilson, J. C., Reeves, J. M., Huey, L. G., Holloway, J. S., Parrish, D. D., Hubler, G., and Fehsenfeld, F. C.: Particle growth in the plumes of coal-fired power plants, J. Geophys. Res., 107, AAC 9, D12, 4155, doi:10.1029/2001JD001062, 2002. 2002.

Bukowiecki, N., Dommen, J., Prévôt, A. S. H., Weingartner, E., and Baltensperger, U.: Fine and ultrafine particles in the Zrich (Switzerland) area measured with a mobile laboratory: an assessment of the seasonal and regional variation throughout a year, Atmos. Chem. Phys., 3, 1477–1494, doi:10.5194/acp-3-1477-2003, 2003.

Carslaw, D.: Evidence of an increasing NO_2/NO_x emissions ratio from road traffic emissions, Atmos. Environ., 39, 4793–4802, 2005.

Casati, R., Scheer, V., Vogt, R., and Benter, T.: Measurements of nucleation and soot mode particle emission from a diesel passenger car in real world and laboratory in situ dilution, Atmos. Environ., 41, 2125–2135, 2007

Cavalli, F., Viana, M., Yttri, K. E., Genberg, J., and Putaud, J.-P.: Toward a standardised thermal-optical protocol for measuring atmospheric organic and elemental carbon: the EUSAAR protocol, Atmos. Meas. Tech., 3, 79–89, doi:10.5194/amt-3-79-2010, 2010.

Charron, A. and Harrison, R. M.: Fine ($PM_{2.5}$) and coarse ($PM_{2.5-10}$) particulate matter on a heavily trafficked London highway: sources and processes, Environ. Sci. Technol., 39, 7768–7776, 2005.

Charron, A., Birmili, W., and Harrison, R. M.: Factors influencing new particle formation at the rural site, Harwell, United Kindom, J. Geophys. Res., 112, D14210, 15, doi:10.1029/2007/JD008425, 2007,

Cheung, H. C., Morawska, L., and Ristovski, Z. D.: Observation of new particle formation in subtropical urban environment, Atmos. Chem. Phys., 11, 3823–3833, doi:10.5194/acp-11-3823-2011, 2011.

Chio, C.-P. and Liao, C.-M.: Assessment of atmospheric ultrafine carbon particle-induced human health risk based on surface area dosimetry, Atmos. Environ., 42, 8575–8584, 2008.

Curtis, J.: Nucleation of atmospheric aerosol particles, C. R. Physique, 7, 1027–1045, 2006.

Dall'Osto, M., Thorpe, A., Beddows, D. C. S., Harrison, R. M., Barlow, J. F., Dunbar, T., Williams, P. I., and Coe, H.: Remarkable dynamics of nanoparticles in the urban atmosphere, Atmos. Chem. Phys. Discuss., 10, 30651–30689, doi:10.5194/acpd-10-30651-2010, 2010.

Department of Transport, UK: http://www.dft.gov.uk, last access: February 2011.

Dirección General de Tráfico, Spain: http://apl.dgt.es/IEST2, last access: February 2011.

Dunn, M. J., Jiménez, J. L., Baumgardner, D., Castro, T., McMurry, P. H., and Smith, J. N.: Measurements of Mexico City nanoparticle size distributions: Observations of new particle formation and growth, Geophys. Res. Lett., 31, L10102, doi:10.1029/2004GL019483, 2004.

Ecoplan (2007): Auswertung Mikrozensus 2005 für den Kanton Bern, Report, Bern: http://www.bve.be.ch/bve/de/index/direktion/ueber-die-direktion/statistik.assetref/content/dam/documents/BVE/GS/de/Abteilung-Gesamtmobilit%C3%A4t_Mikrozensus-Verkehrsverhalten-2005_Kt-BE.pdf, last access: February 2011.

Fernández-Camacho, R., Rodríguez, S., de la Rosa, J., Sánchez de la Campa, A. M., Viana, M., Alastuey, A., and Querol, X.: Ultrafine particle formation in the inland sea breeze airflow in Southwest Europe, Atmos. Chem. Phys. Discuss., 10, 17753–17788, doi:10.5194/acpd-10-17753-2010, 2010.

Fischer, P. H., Hoek, G., van Reeuwijk, H., Briggs, D. J., Lebret, E., van Wijnen, J. H., Kingham, S., and Elliott, P. E.: Traffic-related differences in outdoor and indoor concentrations of particles and volatile organic compounds in Amsterdam, Atmos, Environ, 34, 3713–3722, 2000.

Fruin, S., Westerdahl, T., Sax, C., Sioutas C., and Fine, P. M.: Measurements and predictors of on-road ultrafine particle concentrations and associated pollutants in Los Angeles, Atmos. Environ., 42, 207–219, 2008.

Gao, J., Wang, T., Zhou, X., Wu, W. and Wang, W.: Measurement of aerosol number size distributions in the Yangtze River delta in China: Formation and growth of particles under polluted

conditions, Atmos. Environ., 43, 829–836, 2009.

Guerra, J. C., Rodríguez, S., Arencibia, M. T., and García, M. D.: Study on the formation and transport of ozone in relation to the air quality management and vegetation protection in Tenerife (Canary Islands), Chemosphere, 56, 1157–1167, 2004.

Hämeri, K., Kulmala, M., Aalto, P., Leszczynski, K., Visuri, R., and Hämekoski, K.: The investigation of aerosol particle formation in urban background area of Helsinki, Atmos. Res., 41, 281–298, 1996.

Hamilton, R. S. and Mansfield, T. A.: Airborne particulate elemental carbon: its sources, transport and contribution to dark smoke and soiling, Atmos. Environ., 25, 715–723, 1991.

Harrison, R. M., Deacon, A. R., Jones, M. R., and Appleby, R. S.: Sources and processes affecting concentrations of PM_{10} and $PM_{2.5}$ particulate matter in Birmingham (UK), Atmos. Environ., 31, 4103–4117, 1997.

Harrison, R. M., Yin, J., Mark, D., Stedman, J., Appleby, R. S., Booker, J., and Moorcroft S.: Studies of the coarse particle (2.5–10μm) component in UK urban atmospheres, Atmos. Environ., 35, 3667–3679, 2001.

Harrison, R. M., Jones, A. M., and Lawrence, R. G.: Major component composition of PM_{10} and $PM_{2.5}$ from roadside and urban background sites, Atmos. Environ., 38, 4531–4538, 2004.

Hueglin, C., Buchmann, B., and Weber, R. O.: Long-term observation of real-worls road traffic emisión factors on a motorway in Switzerland, Atmos. Environ, 40, 3696–3709, 2006.

Imhof, D., Weingärtner, E., Prévôt, A. S. H., Ordoñez, C., Kurtenbach, R., Wiesen, P., Rodler, J., Sturm, P., McCrae, I., Ekström, M., and Baltensperger, U.: Aerosol and NO_x emission factors and submicron particle number size distributions in two road tunnels with different traffic regimes, Atmos. Chem. Phys., 6, 2215–2230, doi:10.5194/acp-6-2215-2006, 2006.

Janssen, N. A. H., Van Mansom, D. F. M., Van Der Jagt, K., Harssema, H., and Hoek, G.: Mass concentration and elemental composition of airborne particulate matter at street and background locations, Atmos. Environ., 31, 1185–1193, 1997.

Johnson, G. R., Ristovski, Z. D., Anna, B. D., and Morawska, L.: The hygroscopic behaviour of partially volatilized coastal marine aerosols using the VH-TDMA technique, J. Geophys. Res., 110, D20203, doi:10.1029/2004JD005657, 2005.

Ketzel, M., Wåhlin, P., Kristensson, A., Swietlicki, E., Berkowicz, R., Nielsen, O. J., and Palmgren, F.: Particle size distribution and particle mass measurements at urban,near-city and rural level in the Copenhagen area and Southern Sweden, Atmos. Chem. Phys., 4, 281–292, doi:10.5194/acp-4-281-2004, 2004.

Kittelson, D. B.: Engines and nanoparticles: a review, J. Aerosol Sci., 29, 575–588, 1998.

Klemm, R. J. and Mason, R. M.: Aerosol Research and Inhalation Epidemiological Study (ARIES): air quality and daily mortality statistical modelling-interim results, J. Air Waste Manage., 50, 1433–1439, 2000.

Kulmala, M., Vehkamaki, H., Petaja, T., Dal Maso, M., Lauri, A., Kerminen, V.M., Birmili, W., and McMurry, P. H.: Formation and growth rates of ultrafine atmospheric particles: a review of observations, J. Aerosol Sci., 35, 143–175, 2004.

Lanz, V., Alfarra, A., Baltensperger, U., Burchmann, B., Huegling, C., Szidat, S., Wehrli, M. N., Wacker, L., Weimer, S., Caseiro, A., Puxbaum, H., and Prévôt, A. S. H.: Source attribution of submicron organic aerosols during wintertime inversions by advanced factor analysis of aerosol mass spectra, Environ. Sci. Technol., 42, 214–220, 2008.

Lanz, V. A., Prévôt, A. S. H., Alfarra, M. R., Weimer, S., Mohr, C., DeCarlo, P. F., Gianini, M. F. D., Hueglin, C., Schneider, J., Favez, O., D'Anna, B., George, C., and Baltensperger, U.: Characterization of aerosol chemical composition with aerosol mass spectrometry in Central Europe: an overview, Atmos. Chem. Phys., 10, 10453–10471, doi:10.5194/acp-10-10453-2010, 2010.

Lee, Y. G., Lee, H. W., Kim, M. S., Choi, C. Y., and Kim, J.: Characteristics of particle formation events in the coastal region of Korea in 2005, Atmos. Environ., 42, 3729–3739, 2008.

Li, N., Sioutas, C., Cho, A., Schmitz, D., Misra, C., Sempf, J., Wan, M., Oberley, T., Froines, T., Nel, A. Ultrafine Particulate Pollutants Induce Oxidative Stress and Mitochondrial Damage, Environ. Health Persp., 111, 4–9, 2003.

Maricq, M. M.: Chemical characterization of particulate emissions from diesel engines: A review, Aerosol Sci., 38, 1079–1118, 2007.

Mejía, J. F. and Morawska, L.: An investigation of nucleation events in a coastal urban environment in the Southern Hemisphere, Atmos. Chem. Phys., 9, 7877–7888, doi:10.5194/acp-9-7877-2009, 2009.

Metzger, A., Verheggen, B., Dommen, J., Duplissy, J., Prevot, A. S. H., Weingartner, E., Riipinen, I., Kulmala, M., Spracklen, D. V., Carslaw, K. S., and Baltensperger, U.: Evidence for the role of organics in aerosol particle formation under atmospheric conditions, Proceedings of the National Academy of Sciences of the United States of America, 107(15), 6646–6651, 2010.

Minoura, H. and Takekawa, H.: Observation of number concentrations of atmospheric aerosols and analysis of nanoparticle behavior at an urban background area in Japan, Atmos. Environ., 39, 5806–5816, 2005.

Moore, K. F., Ning, Z., Ntziachristos, L., Schauer, J. J., and Sioutas, C.: Daily variation in the properties of urban ultrafine aerosol-Part I: Physical characterization and volatility, Atmos. Environ., 41, 8633–8646, 2007.

Morawska, L., Thomas, S., Bofinger, N., Wainwright, D., and Neale, D.: Comprehensive characterization of aerosol in a subtropical urban atmosphere particle size distribution and correlation with gaseous pollutants, Atmos. Environ., 32, 2467–2478, 1998.

Morawska, L., Jayaratne, E. R., Mengersen, K., Jamriska, M., and Thomas, S.: Differences in airborne particle and gaseous concentrations in urban aor between weekdays and weekends, Atmos. Environ., 36, 4375–4383, 2002.

Morawska, L., Ristovski, Z., Jayaratne, E. R., Keogh, D. U., and Ling, X.: Ambient nano and ultrafine particles from motor vehicle emissions: Characteristics, ambient processing and implications on human exposure, Atmos. Environ, 42, 8113–8138, 2008.

Müller, T., Henzing, J. S., de Leeuw, G., Wiedensohler, A., Alastuey, A., Angelov, H., Bizjak, M., Collaud Coen, M., Engström, J. E., Gruening, C., Hillamo, R., Hoffer, A., Imre, K., Ivanow, P., Jennings, G., Sun, J. Y., Kalivitis, N., Karlsson, H., Komppula, M., Laj, P., Li, S.-M., Lunder, C., Marinoni, A., Martins dos Santos, S., Moerman, M., Nowak, A., Ogren, J. A., Petzold, A., Pichon, J. M., Rodriquez, S., Sharma, S., Sheridan, P. J., Teinilä, K., Tuch, T., Viana, M., Virkkula, A., Weingartner, E., Wilhelm, R., and Wang, Y. Q.: Characterization and intercomparison of aerosol absorption photometers: result of two

intercomparison workshops, Atmos. Meas. Tech., 4, 245–268, doi:10.5194/amt-4-245-2011, 2011.

Nel, A.: Air pollution-related illness: effects if particles, Science, 308, 804–806, 2005.

Oltmans, S. J. and Levy II, H.: Surface ozone measurements from a global network, Atmos. Environ., 28, 9–24, 1994.

Pakkanen, T. A., Kerminen, V. M., Ojanena, C. H., Hillamo, R. E., Aarnio, P., and Koskentalo, T.: Atmospheric Black Carbon in Helsinki, Atmos. Environ., 34, 1497–1506, 2000.

Park, K., Park, J. Y., Kwak, J., Cho, G. N., and Kim, J.: Seasonal and diurnal variations of ultrafine particle concentration in urban Gwangju, Korea: Observation of ultrafine particle events, Atmos. Environ., 42, 788–799, 2008.

Pérez, C., Sicard, M., Jorba, O., Comerón, A., Baldasano, J. M.: Summertime re-irculations of air pollutants over the north-eastern Iberian coast observed from systematic EARLINET lidar measurements in Barcelona, Atmos. Environ., 38, 3983–4000, 2004.

Pérez, L., Medina-Ramón, M., Künzli, N, Alastuey, A., Pey, J., Pérez, N., Garcia, A., Tobias, A., Querol, X., and Sunyer, J.: Size fractionated particulate matter, vehicle traffic, and case-specific daily mortality in Barcelona (Spain), Environ. Sci. Technol., 43(13), 4707–4714, doi:10.1021/es8031488, 2009.

Pérez, N., Pey, J., Cusack, M., Reche, C., Querol, X., Alastuey, A., and Viana, M.: Variability of Particle Number, Black Carbon, and PM_{10}, $PM_{2.5}$, and PM_1 Levels and Speciation: Influence of Road Traffic Emissions on Urban Air Quality, Aerosol Sci. Technol., 44, 487–499, 2010.

Petzold, A. and Schönlinnes, M.: Multi-angle absorption photometry-a new method for the measurement of aerosol light absorption and atmospheric Black Carbon, J. Aerosol Sci., 35, 421–441, 2004.

Pey, J., Rodríguez, S., Querol, X, Alastuey, A., Moreno, T., Putaud, J. P., and Van Dingenen, R.: Events and cycles of urban aerosols in the western Mediterranean, Atmos. Environ., 42, 9052–9062, 2008.

Pey, J., Querol, X., Alastuey, A., Rodríguez, S., Putaud, J. P., and Van Dingenen, R.: Source apportionment of urban fine and ultrafine particle number concentration in a Western Mediterranean city, Atmos. Environ., 43, 4407–4415, 2009.

Querol, X., Alastuey, A., Puicercus, J.A., Mantilla, E., Miroa, J.V., Lopez-Soler, A., Plana, F., and Artiñano, B. Seasonal evolution of suspended particles around a large coal-fired power station: particulate levels and sources, Atmos. Environ., 32, 1963–1978, 1998.

Querol, X., Alastuey, A., Rodriguez, S., Plana, F., Ruiz, R.C., Cots, N., Massagué, G., and Puig, O.: PM_{10} and $PM_{2.5}$ source apportionment in the Barcelona Metropolitan area, Catalonia, Spain, Atmos. Environ., 35, 6407–6419, 2005.

Qian, S., Sakurai, H., and McMurry, P. H.: Characteristics of regional nucleation events in urban East St. Louis, Atmos. Environ., 41, 4119–4127, 2008.

Rodríguez, S. and Cuevas, E.: The contributions of "minimum primary emissions" and "new particle formation enhancements" to the particle number concentration in urban air, J. Aerosol Sci., 38, 1207–1219, doi:10.1016/j.jaerosci.2007.09.001, 2007.

Rodríguez, S., Querol, X., Alastuey, A., Kallos, G., and Kakaliagou, O.: Saharan dust contributions to PM10 and TSP levels in Southern and Eastern Spain, Atmos. Environ., 35, 2433–2447, 2001.

Rodríguez, S., Van Dingenen, R., Putaud, J. P., Martins-Dos Santos, S., and Roselli, D.: Nucleation and growth of new particles in the rural atmosphere of Northern Italy-relationship to air quality monitoring, Atmos. Environ., 39, 6734–6746, 2005.

Rodríguez, S., Cuevas, E., González, Y., Ramos, R., Romero, P. M., Pérez, N., Querol, X., and Alastuey, A.: Influence of sea breeze circulation and road traffic emissions on the relationship between particle number, Black Carbon, PM_1, $PM_{2.5}$ and $PM_{2.5-10}$ concentrations in a coastal city, Atmos. Environ., 42, 6523–6534, DOI:10.1016/j.atmosenv.2008.04.022, 2008.

Rohrer, F. and Berresheim, H.: Strong correlation between levels of tropospheric hydroxyl radicals and solar ultraviolet radiation, Nature, 442(7099), 184–187, 2006.

Rönkkö, T., Virtanen, A., Vaaraslahti, K., Keskinen, J., Pirjola, L. and Lappi, M.: Effect of dilution conditions and driving parameters on nucleation mode particles in diesel exhaust: Laboratory and on-road study, Atmos. Environ., 40, 2893–2901, 2006.

Sánchez de la Campa, A., de la Rosa, J., Querol, X., Alastuey, A., Mantilla, E.: Geochemistry and origin of PM_{10} in the Huelva region, Southwestern Spain, Environ. Res., 103, 305–316, 2007.

Sandradewi, J., Prevot, A. S. H., Weingartner, E., Schmidhauser, R., Gysel, M., Baltensperger, U.: A study of wood burning and traffic aerosols in an Alpine valley using a multi-wavelength aethalometer, Atmos. Environ., 42, 101–112, 2008.

Schwartz, S. E., Harshvardhan, and Benkovitz, C. M.: Influence of anthropogenic aerosol on cloud optical depth shown in satellite measurements and chemical transport modelling, Proc. Natl Acad. Sci., 99, 1784–1789, 2002.

Shi, Z., Shao, L., Jones, T. P., Whittaker, A. G., Richards, R. J., and Zhang, P.: Oxidative stress on plasmid DNA induced by inhalable particles in the urban atmosphere, Chinese Sci. Bull., 49, 692–697, doi:10.1007/BF03184267, 2004.

Smargiassi, A., Baldwin, M., Pilger, C., Dugandzic, R., and Brauer, M.: Small-scale spatial variability of particle concentration and traffic levels in Montreal: a pilot study, Sci. Total Environ., 338, 243–251, 2005.

Steinbacher, M., Zellweger, C., Schwarzenbach, B., Bugmann, S., Buchmann, B., Ordoñez, C., Prévôt, A.S.H., and Hueglin, C.: Nitrogen oxide measurements at rural sites in Switzerland: Bias of conventional measurement techniques, J. Geophys. Res., 112, D11307, doi:10.1029/2006JD007971, 2007.

Stolzel, M., Breitner, S., Cyrys, J., Pitz, M., Wölke, G., Kreyling, W., Heinrich, J., Wichmann, H. E., and Peters, A.: Daily mortality and particulate matter in different size classes in Erfurt, Germany, J. Exp. Sc. Environ. Epidemiol., 17, 458–467, 2007.

Swiss Federal Statistical Office: http://www.bfs.admin.ch, last access: February 2011.

Szidat, S., Prevot, A. S. H., Sandradewi, J., Alfarra, M. R., Synal, H.-A., Wacker, L. and Baltensperger U.: Dominant impact of residential wood burning on particulate matter in Alpine valleys during winter, Geophys. Res. Lett., 34, L05820, doi:10.1029/2006GL028325, 2007.

Tiresia: www.tiresia.ch, last access: February 2011.

Turpin, B. J. and Huntzicker, J. J.: Identification of secondary organic aerosol episodes and quantification of primary and secondary organic aerosol concentrations during SCAQS, Atmos.Environ., 29, 3527–3544, 1995.

Van Dingenen, R., Raes, F., Putaud, J.P., Baltensperger, U., Charron, A., Facchini, M.C., Decesari, S., Fuzzi, S., Gehrig, R.,

Hansson, H. C. Harrison, R. M., Hüglin, C., Jones, A. M., Laj, P., Lorbeer, G., Maenhout, W., Palmgren, F., Querol, X., Rodriguez, S., Schneider, J., Brink, H., Tunved, P., Tørseth, K., Wehner, B., Weingartner, E., Wiedensohler, A., Whlin, P. : A European aerosol phenomenology – 1: physical characteristics of particulate matter at kerbside, urban, rural and background sites in Europe, Atmos. Environ., 38, 2561–2577, 2004.

Viana, M., Querol, X., Alastuey, A., Cuevas, E., andRodríguez, S.: Influence of African dust on the levels of atmospheric particulates in the Canary Islands air quality network, Atmos. Environ., 36, 5861–5875, 2002.

Von Klot, S., Wolke, G., Tuch, T., Heinrich, J., Dockery, D.W., Schwartz, J., Kreyling, W.G., Wichmann, H. E., andPeters, A.: Increased asthma medication use in association with ambient fine and ultrafine particles, Eur. Respir. J., 20, 691–702, 2002.

Watson, J. G., Chow, J. C., Lowenthal, D. H., Pritchett, L. C., Frazier, C. A., Neuroth, G. R., and Robbins, R.: Differences in the carbon composition of source profiles for diesel- and gasolinepowered vehicles, Atmos. Environ., 28(15), 2493–2505, 1994.

Weber, R. J., Marti, J. J., McMurry, P. H., Eisele, F. L., Tanner, D. J., and Jefferson, A.: Measurements of new particle formation and ultrafine particle growth rates at a clean continental site, J. Geophys. Res., D102, 4375–4385, 1997.

Wehner, B., Birmili, W., Gnauk, T., and Wiedensohler, A.: Particle number size distribution in a street canyon and their transformation into the urban-air background: measurements and a simple model study, Atmos. Environ., 36, 2215–2223, 2002.

Wehner, B., Uhrner, U., von Löwis, S., Zallinger, M., and Wiedensohler, A.: Aerosol number size distributions within the exhaust plume of a diesel and a gasoline passenger car under on-road conditions and determination of emission factors, Atmos. Environ., 43, 1235–1245, 2009.

Wikipedia: http://en.wikipedia.org/wiki/London, last access: January 2011, 2010.

Wichmann, H. E., Spix, C., Tuch, T., Wölke, G., Peters, A., Heinrich, J., Kreyling, W. G., and Heyder, J.: Daily Mortality and Fine and Ultrafine Particles in Erfurt, Germany, Part I: Role of Particle Number and Particle Mass, HE Publications, 98, 2000.

Zhang, K. M., Wexler, A. S., Zhu, Y. F., Hinds, W. C., and Sioutas, C.: Evolution of particle number distribution near roadways, Part II: the "Road-to-Ambient" process, Atmos. Environ., 38, 6655–6665, 2004.

Zhu, Y., Hinds, W. C., Kim, S., Shen, S., and Sioutas, C.: Study of ultrafine particles near a major highway with heavy-duty diesel traffic, Atmos. Environ., 36, 4323–4335, 2002

Zong-bo, S., Ke-bin, H., Xue-chun, Y., Zhi-liang, Y., Fu-mo, Y., Yong-liang, M., Rui, M., Ying-tao, J., and Jie, Z.: Diurnal variation of number concentration and size distribution of ultrafine particles in the urban atmosphere of Beijing in winter, J. Environ. Sci., 19, 933–938, 2007.