Sources and processes affecting urban aerosols in a coastal Mediterranean environment

Doctoral dissertation

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ABSTRACT

Air pollution is a major public health concern causing annually an estimated 380000 premature deaths in the European Union alone. A number of epidemiological studies carried out during recent decades have associated atmospheric particulate matter (PM) with cardiovascular and respiratory morbidity and mortality. Thus, investigation of the sources and mechanisms responsible for increasing PM concentrations in urban environments has become one of the most important fields of research in environmental sciences.

The sources, dispersion and chemical processes governing air quality vary in each European region, so that, for example conclusions regarding atmospheric particle contamination reported for central and northern European cities cannot necessarily be directly applied to the Mediterranean area, where information on the number and size distribution of particles and chemical speciation PM data are relatively scarce. In this context, the study presented in this thesis offers an unprecedentedly detailed investigation of the processes and sources affecting atmospheric pollutants at an urban background site in the coastal Mediterranean city of Barcelona.

Road traffic is the most important particle source in Barcelona, with exhaust emissions representing about 40-45% of the PM_1 mass. It governs the time variation of Black Carbon (BC) levels, which may be proposed as a vehicle exhaust emissions tracer to be added to urban air quality control networks. Study of the BC/CO, BC/NO_2 and BC/NO ratios in different European urban environments evidenced the variability of these ratios as a function of the specific characteristic of each site, such as the distance to traffic, vehicle fleet composition and age and the influence of other carbonaceous sources, such as biomass burning.

The evaluation of the coarse aerosol ($PM_{2.5-10}$) daily cycle during an intensive sampling campaign (DAURE) evidenced the influence of construction-demolition works. These activities increased hourly $PM_{2.5-10}$ levels by up to 8 $\mu g\ m^{-3}$ on an annual mean basis based on hourly averages. Although the mineral matter content of this source is similar to traffic resuspension, regional dust or Saharan dust, and it was therefore not possible to discriminate construction/demolition particles in a distinct way, the time variation of coarse Ca and S (tracers of construction works), allowed us to demonstrate the impact of these activities on the PM coarse fraction in our measurements.

Particle number (N) data were analysed during the DAURE campaign in search for the primary emissions of vehicle exhaust (N1) and the secondary particles from gaseous precursors, primary particles from non-traffic sources, and/or particles inherited in the air mass (N2). This analysis was based on the relation between N and BC. The N2 fraction accounted for 40% of number concentrations, ranging from 37% during the morning rush hour to 61% at midday. This high contribution of N2 during midday prompted us to carry out further analysis using data collected during the whole of 2009, comparing the results in Barcelona with those collected in five other European cities in different regions. This study allowed us to conclude that the midday N peak was only observed in southern European cities, which at that time of day is controlled by: 1) higher solar radiation, 2) higher temperature and 3) a contribution of SO_2 from shipping and industry governed by the breeze circulation, all of this resulting in enhanced nucleation processes at these latitudes, giving rise to high particle number concentrations.

The significant contribution of secondary inorganic aerosols to PMx mass detected in Barcelona, higher than in other European cities with similar NOx and SO_2 levels, motivated a study of the levels and sources of NH_3, the main precursor of these new formed particles. Passive samplers were used in order to cover a large area of the city in summer and winter, proving higher levels during summer. During this season levels were well above those reported in other European cities. Waste containers were found to be the main source responsible for the high levels, although an important local contribution from traffic emissions was also detected.

The highest NH_3 levels were mostly registered in the historic city centre, which is located to the south of the monitoring site, in an area closest to the sea from where the wind typically transports pollutants at midday. This transport of NH_3, the main precursor of particles through reactions with sulphuric and nitric acids, could also partly explain the N midday peak associated with secondary inorganic aerosol formation.

An annual contribution from regional-scale biomass burning emissions was detected and quantified for the fist time in Barcelona by means of specific tracers, namely Levoglucosan, K^+ and OC, and the application of a special-purpose Multilinear Engine-2 (ME-2) script. It results in a contribution of 3% to PM_{10} and $PM_{2.5}$ and 5% to PM_1, much lower than those calculated for other northern and central European cities. A regional-scale origin of this contribution was concluded, as it showed a characteristic hourly trend with night-time maxima, coinciding with the land-to-sea breeze.

Finally, the study was broadened to evaluate the exposure risk and toxicology of $PM_{2.5-10}$ and $PM_{0.1-2.5}$ using a multidisciplinary approach to obtain an estimation of the health impact of the different emission sources of Barcelona. Two different tests were performed to characterise the oxidative stress generation capacity of the samples, obtaining similar results than those reported in other urban sites with intense metal emissions. Results concerning the ROS-generation capacity were correlated with the ones obtained from a cancer risk assessment of the different PM sources detected in Barcelona by means of the receptor model Positive Matrix Factorization (PMF) and a ME-2 script, attaining a high correlation factor for the $PM_{0.1-2.5}$ particles. This health risk estimation underestimated the impact of road traffic since only the particulate phase of urban emissions was considered, with the lack of VOCs measurements, which are expected greatly to increase the cancer risk of the exhaust emissions. Finally, four months of on-line measurements of the lung deposited surface area (LDSA) revealed a high correlation factor between this parameter and BC, pointing at traffic as the major factor responsible for daily variation of LDSA in the city of Barcelona.

RESUMEN

La contaminación atmosférica es un problema de salud pública que causa más de 380000 muertes sólo en la Unión Europa. Un número importante de estudios epidemiológicos llevados a cabo en las últimas décadas ha asociado el material particulado atmosférico (PM) con la mortalidad y la morbilidad de origen respiratorio y cardiovascular. Así, la investigación sobre las fuentes y mecanismos implicados en esta asociación es hoy en día uno de los campos más relevantes en ciencias ambientales.

Las fuentes de emisión y los procesos fisico-químicos que rigen la calidad del aire varían ampliamene de una región Europea a otra, por lo que las conclusiones sobre los procesos y fuentes de partículas atmosféricas obtenidas para ciudades del centro y norte de Europa no pueden ser directamente aplicadas al área del Mediterráneo, donde existe escasa información a escala urbana sobre el número y la distribución de tamaños de partículas, y sobre datos en tiempo real de especiación química.

Para este estudio, se investigó en profundidad una estación de fondo urbano situada en la ciudad de Barcelona, en la costa Mediterránea. Para ello, se contó con una extensa instrumentación que proporcionó datos sobre niveles y composición de PM con una alta resolución temporal que nos permitió aportar nuevos conocimientos sobre los principales procesos y fuentes que afectan a los contaminantes atmosféricos en esta zona.

El tráfico rodado es la fuente más importante de partículas en Barcelona, con las emisiones del tubo de escape representando alrededor del 40-45% de la masa de PM_1. Esta fuente rige la variación de los niveles de Black Carbon (BC), parámetro que proponemos como un preciso trazador de este tipo de emisiones y que debería ser incluido en las redes de control de calidad del aire. El análisis de los ratios BC/CO, BC/NO_2 y BC/NO en diferentes ambientes urbanos europeos mostró una dependencia de estos valores de las características específicas de cada zona de estudio, variando con la distancia al tráfico, la composición y antigüedad del parque de vehículos y la posible influencia de otras fuentes de naturaleza carbonosa, como la quema de biomasa.

La evaluación de la variación horaria del aerosol grueso ($PM_{2.5-10}$) durante la intensiva campaña internacional DAURE suministró evidencias acerca del impacto de los trabajos de construcción y demolición en la calidad del aire. Estas actividades podrían aumentar hasta en 8µg m^{-3} los niveles horarios de $PM_{2.5-10}$ considerando valores medios anuales. A pesar de que el contenido mineral de esta fuente es similar al presente en el material resuspendido por tráfico, en el material de origen regional o en el

de las intrusiones saharianas, y que no es posible asociar todo el incremento de la fracción $PM_{2.5-10}$ a las particulas resuspendidas por el viento procedentes de estas actividades, la variación horaria de Ca y S en la fracción gruesa (considerados los principales trazadores de los trabajos de construcción en estudios anteriores), permitió demostrar el impacto de este tipo de actividades en nuestras mediciones.

Los datos sobre el número de partículas (N) fueron analizados durante la campaña DAURE, estudiando la relación entre las concentraciones de N y BC, y dividiendo N en dos componentes (N=N1+N2) mediante el uso de la pendiente mínima entre ambos parámetros. N1 representa las emisiones procedentes de los tubos de escape, más concretamente emisiones de material carbonoso y de determinados compuestos que nuclean/condensan inmediatamente tras su entrada en el aire ambiente. N2 se define como la componente que constituye la fracción secundaria de partículas formadas a partir de precursores gaseosos, la fracción primaria de fuentes diferentes al tráfico y/o partículas heredadas en la masa de aire. N2 representa el 40% de la concentración en número, variando del 37% durante las horas matinales de tráfico hasta el 61% al mediodía. Esta elevada contribución durante las horas centrales del día nos llevó a realizar el mismo anális usando datos recogidos durante todo el año 2009 y comparando los resultados obtenidos en Barcelona con aquellos recogidos en otras cinco ciudades Europeas. Esta comparación permitió concluir que el máximo de N a mediodía sólo se observaba en ciudades del sur de Europa, que en las horas centrales del día cuentan con: 1) alta radiación solar, 2) altas temperaturas y 3) una contribución de SO_2 procedente de la industria y/o de los barcos regida por la circulación de la brisa, todo esto resultando en un incremento de los procesos de nucleación en estas latitudes que dan lugar a un número elevado de partículas.

La importante contribución de aerosoles inorgánicos secundarios a la masa de PM_X, mayor que en otras ciudades europeas con niveles similares de NO_X y SO_2, motivó el estudio de las concentraciones y fuentes de NH_3. Se utilizaron dosímetros pasivos para cubrir una extensa área de la ciudad de Barcelona durante las estaciones de verano e invierno, obteniendo concentraciones muy elevadas durante verano. En esta estación los niveles estuvieron muy por encima de aquellos medidos en otras ciudades europeas. Los contenedores de basura fueron el mayor responsable de los altos niveles, aunque también se detectó un impacto considerable procedente de las emisiones del tráfico.

Los niveles más altos de NH_3 fueron mayoritariamete registrados en el centro histórico de la ciudad, situado en el sur de Barcelona, en un área cercana a la costa, desde donde el viento típicamente transporta los contaminantes durante las horas centrales del día. Este transporte de NH_3, el principal precursor de partículas en la atmósfera a través de la reacción con los ácidos de azufre y nitrógeno, podría explicaR al menos parcialmente el máximo de N a mediodía asociado con la formación de aerosoles inorgánicos secundarios.

La contribución anual de quema de biomasa al PM a escala regional fue detectada y cuantificada por primera vez en Barcelona a partir de trazadores específicos, concretamente Levoglucosan, K^+ y OC, y la aplicación del modelo receptor Positive Matrix Factorization (PMF) y el programa Multilinear Engine 2 (ME-2). Este análisis resultó en una estimación del 3% para la contribución de quema de biomasa al PM_{10} y al $PM_{2.5}$ y del 5% al PM_1, estos porcentajes están muy por debajo de los obtenidos para otras ciudades del centro y norte de Europa. Se concluyó que la contribución tenía un origen regional, ya que mostró una tendencia horaria característica con máximos en el periodo nocturno, coincidiendo con la brisa tierra-mar.

El riesgo de exposición y la toxicología de las partículas en las fracciones $PM_{2.5\text{-}10}$ y $PM_{0.1\text{-}2.5}$ se evaluó mediante un enfoque multidisplinar para obtener una estimación del impacto en la salud de las diferentes fuentes de emisión de Barcelona. Se llevaron a cabo dos tipos de ensayo complementarios para caracterizar la capacidad de generar estrés oxidativo de las diferentes muestras de PM, obteniendo resultados similares a aquellos concluidos para otros ambientes urbanos con altas emisiones de metales. Los resultados de estos ensayos se correlacionaron con los obenidos de la evaluación de riesgo de cáncer de las diferentes fuentes de emisión detectadas en Barcelona a partir del modelo receptor PMF y el programa ME-2, encontrándose un factor de correlación significativo para la fracción $PM_{0.1\text{-}2.5}$. Esta estimación de riesgo subestimó el impacto del tráfico ya que sólo se tuvo en cuenta la fracción particulada de las emisiones urbanas, dada la no disponibilidad de medidas de las concentraciones de VOCs, que se espera que puedan elevar el riesgo de cancer estimado para las emisiones de los tubos de escape.

Asimismo, se tomaron cuatro meses de medidas en tiempo real de superficie específica de las partículas que depositadas en el pulmón, que dificultan el intercambio gaseoso (lung deposited surface area, LDSA), obteniendo una correlación muy significativa con las concentraciones de BC, señalando así al tráfico como el principal responsable de la variación diaria de este parámetro en Barcelona y por lo tanto, de potenciales efectos negativos respiratorios.

RESUM

La contaminació atmósferica és un problema de salut pública que causa més de 380000 morts només a la Unió Europea. Un nombre important d'estudis epidimiològics durts a terme en els últims anys ha associat el material particulat atmosfèric (PM) amb la mortalitat i la morbilitat d'origen respiratori i cardiovascular. Així mateix, la investigació al voltant de les fonts i mecanismes implicats en aquesta associació és avui dia un dels camps més relevants en les ciències ambientals.

Les fonts d'emissió i els processos fisicoquímics que regeixen la qualitat de l'aire varien ampliamene d'una regió europea a una altra, de manera que les conclusions sobre processos y fonts de particules atmosfèriques obtingudes per a ciutats del centre i nord d'Europa no poden ser directament aplicades a l'àrea del Mediterrani, on hi ha escassa informació a escala urbana sobre el nombre i la distribución de mides de particules i sobre dades en temps real d'especiació química.

Per a aquest estudi, es va investigar en profunditat una estació de fons urbà situada a la ciutat de Barcelona, pertanyent a la costa Mediterrània. Per a això, es va comptar amb una extensa instrumentació que va proporcionar dades sobre nivells i composició de PM amb una alta resolució temporal que va permetre aportar nous coneixements sobre els principals processos i fonts que afecten els contaminants atmosfèrics en aquesta zona.

El trànsit rodat és la font més important de partícules a Barcelona, amb les emissions del tub d'escapament representant al voltant del 40-45% de la massa de PM_1. Aquesta font regeix la variació dels nivells de Black Carbon (BC), paràmetre al qual proposem com un precís traçador d'aquest tipus d'emissions i que ha de ser inclòs en les xarxes de control de qualitat de l'aire. L'anàlisi de les ràtios BC/CO, BC/NO_2 i BC/NO en diferents ambients urbans europeus va mostrar una dependència d'aquests valors de les característiques especifiques de cada zona d'estudi, variant amb la distància al trànsit, la composició i antiguitat del parc de vehicles i la possible influència d'altres fonts de naturalesa carbonosa, com la crema de biomassa.

L'avaluació de la variació horària de l'aerosol gruix ($PM_{2.5-10}$) durant la intensiva campanya internacional DAURE va suministrar evidències de l'impacte dels treballs de construcció i demolició en la qualitat de l'aire. Aquestes activitats podrien augmentar fins a 8µgm^{-3} els nivells horaris de $PM_{2.5-10}$ considerant valors mitjans anuals. Tot i que el contingut mineral d'aquesta font és similar al present en el material resuspès per trànsit, en el material d'origen regional o en el de les intrusions saharianes, i que no és possible associar tot l'increment de la fracció $PM_{2.5-10}$ a les partícules resuspeses pel

vent procedents d'aquestes activitats, la variació horària de Ca i S a la fracció gruixuda, considerats els principals traçadors dels treballs de construcció en estudis anteriors, permet demostrar l'impacte d'aquest tipus d'activitats.

Les dades sobre el nombre de partícules (N) van ser analitzats durant la campanya DAURE, estudiant la relació entre les concentracions de N i BC, i dividint N en dos components (N = N1 + N2) mitjançant l'ús de la pendent mínima entre ambdós paràmetres. N1 representa les emissions procedents dels tubs d'escapament, més concretament emissions de material carbonós i de determinats compostos que nuclean/condensen immediatament després de la seva entrada en l'aire ambient. N2 es defineix com la component que constitueix la fracció secundària de partícules formades a partir de precursors gasosos, la fracció primària de fonts diferents al trànsit i/o partícules heretades en la massa d'aire. N2 representa el 40% de la concentració en nombre, variant del 37% durant les hores matinals de trànsit fins el 61% al migdia. Aquesta elevada contribució durant les hores centrals del dia ens va portar a realitzar el mateix analistes utilitzant dades recollides durant tot l'any 2009 i comparant els resultats obtinguts a Barcelona amb aquells recollits en altres cinc ciutats europees. Aquesta comparació va permetre concloure que el màxim de N al migdia només s'observava en ciutats del sud d'Europa, que en les hores centrals del dia disposen de: 1) alta radiació solar, 2) altes temperatures i 3) una contribució de SO_2 procedent de la indústria i dels vaixells regida per la circulació de la brisa, tot això resultant en un increment dels processos de nucleació en aquestes latituds que donen lloc a un nombre elevat de partícules.

La important contribució d'aerosols inorgànics secundaris a la massa de PM_X, més gran que en altres ciutats europees amb nivells similars de NO_X i SO_2, va motivar l'estudi de les concentracions i fonts de NH_3. Es van utilitzar dosímetres passius per tal de cobrir una extensa àrea de la ciutat de Barcelona durant les estacions d'estiu i hivern, obtenint concentracions molt elevades durant l’estiu. En aquesta estació els nivells van estar molt per sobre d'aquells mesurats en altres ciutats Europees. Els contenidors d'escombraries van ser el major responsable dels alts nivells, encara que també es va detectar un impacte considerable procedent de les emissions del trànsit.

Els nivells més alts de NH_3 foren mayoritariamete registrats al centre històric de la ciutat, situat al sud de Barcelona, en una àrea propera a la costa, des d'on el vent típicament transporta els contaminants durant les hores centrals del dia. Aquest transport de NH_3, el principal precursor de partícules en l'atmosfera a través de la reacció amb els àcids de sofre i nitrogen, podria explicar al menys parcialment el màxim de N al migdia associat amb la formació d'aerosols inorgànics secundaris.

La contribució anual de crema de biomassa al PM a escala regional va ser detectada quantificada per primer cop a Barcelona a partir de traçadors específics, concretament Levoglucosan, K^+ i OC i l'aplicació del model Multilinear Engine 2 (ME-2). Aquesta anàlisi va resultar en una estimació del 3% per la contribució de crema de biomassa al PM_{10} i al $PM_{2.5}$ i del 5% al PM_1, aquests percentatges estan molt per sota dels obtinguts per altres ciutats del centre i nord d'Europa. Es va concloure que la contribució tenia un origen regional, ja que va mostrar una tendència horària característica amb màxims en el període nocturn, coincidint amb la brisa terra-mar.

El risc d'exposició i la toxicologia de les partícules en les fraccions $PM_{2.5\text{-}10}$ i $PM_{0.1\text{-}2.5}$ es va avaluar mitjançant un enfocament multidisciplinar per obtenir una estimació de l'impacte en la salut de les diferents fonts d'emissió de Barcelona. Es van dur a terme dos tipus d'assaig complementaris per caracteritzar la capacitat de les diferents mostres de PM de generar estrès oxidatiu, obtenint resultats similars a aquells conclosos per altres ambients urbans amb altes emissions de metalls. Els resultats d'aquests assaigs es van correlacionar amb els obenidos de l'avaluació de risc de càncer de les diferents fonts d'emissió detectades a Barcelona a partir del model receptor Positive Matrix Factorization (PMF) i el programa ME-2, trobant-se un factor de correlació significatiu per la fracció $PM_{0.1\text{-}2.5}$. Aquesta estimació de risc subestima l'impacte del trànsit ja que només es va tenir en compte la fracció particulada de les emissions urbanes, donada la no disponibilitat de mesures de les concentracions de VOCs, que s'espera que puguin elevar el risc de càncer estimat per a les emissions dels tubs d'escapament.

A més, es van prendre quatre mesos de mesures en temps real de la superficie específica de les particules que dipositades al pulmó dificulten l'intercanvi gasós (lung deposited surface area, LDSA), obtenint una correlació molt significativa amb les concentracions de BC, assenyalant així al trànsit com el principal responsable de la variació diària d'aquest paràmetre en Barcelona.

CHAPTER 1: Introduction

1. INTRODUCTION

Air pollution problems are not something new. In the 3rd Century BC an Aristotle student stated that "smell of burning coal was disagreeable and troublesome" and the Roman philosopher, Seneca, already wrote of the heavy air of Rome in 61 AD. The growth of population areas coupled with the switch from wood-burning to coal-burning fires created clouds of smoke over cities as early as the eleventh century. Air pollution regulations first appeared in England in 1273, but for the next several centuries, attempts to control the burning of coal met notable failure. As the Industrial Revolution swept across countries, and as coal became common in private residences, smoke and industrial pollution claimed more and more lives. In 1948 in the United States (Donora, Pennsylvania) twenty people died and 7,000 were hospitalized with respiratory problems and between December 5th and 9th 1952, 4,000 people died in London as a result of smog from burning poor quality coal trapped in a thermal inversion. Table 1.1 summarizes the most important air pollution disasters recorded during the last century, showing a change in sources and, therefore, a change in the concerning pollutants to be controlled in the cities. The data from Table 1.1 highlights the importance of atmospheric particulate matter given the increased use of vehicles and the decrease of industrial sources in urban environments in recent decades.

Table 1.1. Air pollution episodes recorded during the last century (adapted from EPA, 2010).

	Meuse Valley, Belgium (1930)	**Donora, USA (1948)**	**Pozo Rico, Mexico (1950)**	**London, UK (1952)**	**Bhopal, India (1984)**	**London, UK (1991)**
Excess deaths	60	15	20	4000	2500	180
Excess hospitalized	6000	5900	-	>20000	10000	-
Age groups affected	elderly	elderly	all ages	elderly at first	-	patients with respiratory problems
Weather	anticyclonic inversion and fog	anticyclonic inversion and fog	nocturnal inversion, low winds	anticyclonic inversion and fog	nocturnal inversion, low winds	anticyclonic inversion and fog
Geographical setting	river valley	river valley	Coastal	river plain	-	river plain
Sources	steel and zinc manufacture	steel and zinc manufacture	sulphur recovery (accident)	domestic coal burning	fracturing of tank (accident)	vehicles
Pollutants	SO_2, smoke	SO_2, smoke	H_2O	SO_2, smoke, metals	methyl-isocyanide	NO_2, particles

1.1.PARTICULATE MATTER COMPOSITION AND SOURCES

Atmospheric particulate matter (PM) is made up of liquid or solid particles suspended in the atmosphere (Mészáros, 1999). A proportion of the particles are emitted directy into the atmosphere from emission sources (primary particles), while others come into being in the air by gas-to-particle conversion (secondary particles) (Mészáros, 1999). The term aerosol is generally identified with PM, although it also includes the air mass transporting the particles (Putaud et al., 2004).

As atmospheric particles originate from a variety of sources, they possess a range of morphological, chemical, physical, and thermodynamic properties. Examples include combustion-generated particles such as diesel soot or fly ash, photochemically produced particles such as those found in urban haze, salt particles formed from sea spray, and soil-like particles from resuspended dust. They mostly contain inorganic ions, metallic compounds, elemental carbon (EC), organic compounds, and crustal compounds.

PM is a ubiquitous component of the atmosphere, given that is released by several natural sources (soil re-suspension, sea spray, volcanic ash, forest fires, etc.) and can be transported by wind for long distances. It is indispensable for cloud condensation and rainfall production. Human activities contribute to increase locally and regionally the levels of PM in the atmosphere, although at a global scale, natural sources are dominant (IPCC, 2007). Main anthropogenic sources include transport, power generation, industrial activities, construction and demolition works, mining activities, agriculture and biomass burning. Regardless of its origin, PM is considered as an atmospheric pollutant, since the alteration that provokes on the regional composition of atmosphere can cause harm or discomfort to humans and damages to the natural environment (Mészáros, 1999).

PM varies in size, number, shape, surface area, chemical composition, solubility, redox activity, and origin. Aerodynamic diameter is a physical property of a particle in a viscous liquid such as air. It expresses the diameter of a perfect sphere with unit-density and same terminal settling velocity of the given irregular particle. It is important for particle transport, removal, collection, and respiratory tract deposition. PMs is generally categorized according to its diameter, with the most common categories including Total Suspended Particles (TSP) which include all particles up to some 30 μm in diameter; PM_{10} which includes particles with an aerodynamic diameter of less than or equal to 10 μm; $PM_{2.5-10}$, which includes particles with a diameter between 2.5 μm and 10 μm, referred to as “coarse particles”; $PM_{2.5}$ which includes particles with a diameter of less than or equal to 2.5 μm referred to as “fine particles”; PM_1 which include particles with a diameter of less than or equal to 1 μm sometimes referred to as “very fine particles”; and $PM_{0.1}$ which include particles with a diameter of less than 0.1 μm (typically in the size range of 1 to 100 nanometers) referred to as “ultrafine particles” (UF). The level of PM pollution is commonly described in terms of the total number or total mass of the particles by unit gas volume (number or mass concentration). The dimension of the number concentration is generally cm^{-3} (more exactly particles cm^{-3}), while the mass concentration is expressed mainly in $\mu g\ m^{-3}$. Both number and mass concentration vary in space and time as a function of the interaction of sources and sinks.

Once emitted, the evolution of atmospheric aerosols in the environment is affected by processes such as dilution, coagulation, condensation evaporation and deposition, which modify the number and/or the size distribution, and that are influenced by meteorological parameters such as temperature, relative humidity, wind speed, or insolation. The effect of these processes affecting the number and size distribution of fine and ultrafine aerosols has been studied in detail in Northern and Central Europe (Nilsson and Kulmala, 1998; Wehner et al., 2002; Ketzel et al., 2004; Rose et al., 2006; Olivares et al., 2007), but this kind of studies is scarcer in southern Europe, especially in the Mediterranean area (Van Dingenen et al., 2004; Rodríguez et al., 2005; Rodriguez and Cuevas, 2007; Sorribas et al., 2007; Pey et al., 2009; Fernández-Camacho et al., 2010).

The study of airborne PM is an area of research interest owing to the recognized implications for human health, increasing risk of morbidity and mortality (Miller et al, 2007; Dockery and Stone, 2007; WHO, 2006; Brunekreef and Forsberg, 2005; Pope et al., 2002 and 2004; Wichmann et al., 2000; Schwartz et al., 1994; Dockery et al., 1993) and potential influences on climate (IPCC, 2007).

1.2. THE CONTRIBUTION OF PRIMARY PARTICLES

Primary particles are emitted directly into the atmosphere from natural sources such as volcanoes, forest fires, sea spray, and windborne dust, and anthropogenic sources such as fossil fuel burning in combustion engines and power plants. Primary particles occur in the ultrafine, fine and coarse modes.

Ultrafine primary particle emissions are especially important in urban areas, where road traffic is the most important emission source. They tend to exhibit a size distribution with a “nucleation mode (<30nm)” and an “Aitken or carbonaceous mode (50 to >100nm)” (Casati, et al., 2007; Harris and Maricq, 2001). Heavy duty engines may also emit carbonaceous particles in the accumulation and supermicron ranges (Morawska, et al., 1998). The formation of the primary nucleation mode “during the emission, dilution, cooling and mixing of the exhaust with the ambient air" is favoured by several factors depending on the "technology of the vehicle" (such as a high sulphur content in the fuel or the type of oil lubricant used in the engine) and the "ambient air conditions" (such as low winter ambient temperature, or low dilution after the emission; Casati et al., 2007; Shi et al., 1999). This latter point implies that the amount of new particles formed in the vehicle exhaust may experience significant variations depending on the ambient air conditions. For example, in Stockholm it was observed how the slope of the particle number versus NOx concentrations increased when the ambient air temperature decreased (Gidhagen et al., 2005). These "fresh nucleation particles in the vehicle exhaust" are mostly constituted by sulphuric acid and organic compounds and are frequently one of the most important fractions in terms of number concentration (Kittelson, 1998). Particles also evaporate semi-volatile OM that yield to very reactive semi volatile organic compounds (SVOC) which will in turn condensate producing a large proportion of OM in PM (Robinson et al., 2007; Dall'Osto et al., 2011).

The contribution of ultrafine particles has been estimated in about 55% to total number concentration at rush hours in Santa Cruz de Tenerife (Rodriguez and Cuevas, 2007) and in 40% in Huelva (Fernández-Camacho et al., 2010). These particles emissions are estimated to contribute about 55% of global cloud condensation nuclei (CCN) number concentrations at 0.2% supersaturation in the boundary layer (BL), and up to 70% in polluted continental regions (Merikanto et al., 2009).

Coarse particles are mainly primary and generated by mechanical processes from a variety of sources. Natural origin particles are mineral dust resupended and transported from arid areas, sea spray at coastal sites and biogenic compounds. In urban areas road traffic, construction and demolition activities and combustion are also important sources of anthropogenic primary coarse particles.

1.3. THE CONTRIBUTION OF SECONDARY PARTICLE FORMATION

Understanding the effects of atmospheric aerosol particles on human health and the environment, and developing strategies for controlling particle concentrations, require investigating the kinetics, products, and mechanisms of gas-phase reactions by which key atmospheric oxidants convert the major classes of atmospheric gases to condensable species, and also the heterogeneous (surface or liquid phase) reactions involved in gas-to-particle conversion.

The contribution of secondary aerosols formed from atmospheric gas-phase species to the total amount of PM is very important in many urban and remote areas (Seinfeld and Pandis, 1998; Finlayson-Pitts and Pitts Jr., 2000). It has been estimated in about 45-60% (Putaud et al., 2004; Viana et al., 2008). Secondary aerosols consist of inorganic and organic components and, with very few exceptions aerosol formation events always occurr during daytime given that photochemistry plays a central role in their formation process (e.g. Wiedensohler et al., 1997; Vehkamäki et al., 2004; Suni et al., 2008). Other factors that favour atmospheric aerosol formation include a sufficiently low pre-existing aerosol concentration and high vapour source rate e.g. via biogenic emissions. In an atmosphere with high levels of pollutants, condensation and coagulation processes are favoured over nucleation (new particle formation).

Secondary inorganic aerosols (SIA) contribute a large part of the particulate mass in Europe (e.g. Putaud et al., 2004) and include ammonium nitrate and ammonium sulphate. The equilibrium between ammonium nitrate and its gaseous precursors is relatively well understood (e.g. Basset and Seinfeld, 1983; Nenes et al., 1998; Zhang et al., 2000). The gas-aerosol partitioning of nitrate depends strongly on the availability of its precursor gasses and on the ambient conditions (Ansari and Pandis, 1998). Atmospheric ammonia is first neutralized by sulphuric acid (H_2SO_4) to form ammonium sulphate ($(NH_4)_2SO_4$) and the remaining ammonia may then combine with nitric acid to form ammonium nitrate. Model sensitivity studies have shown that under conditions where ammonia limits the formation of nitrate a decline in sulphate concentrations may result in a subsequent rise of the nitrate levels (Ansari and Pandis, 1998; West et al., 1999; Metzger et al., 2002).

Sulphuric acid vapour is a key contributor to secondary new aerosol formation by nucleation, however, variations in sulphuric acid levels do not account for all the variability in observed nucleation rates. Theory suggests that nucleation of sulphuric acid aerosols, even with the help of condensing water vapour, should not occur under conditions near the Earth's surface. Instead, small clusters of sulphuric acid molecules should evaporate, rather than survive as new particles (Kulmala and Kerminen, 2008). Thus, other factors must be involved. Measurements and theory have shown that the presence of ammonia and some organic compounds can increase nucleation rates when they join small clusters of sulphuric acid molecules (Kirkby et al., 2011).

Interest on urban levels of ammonia (NH_3) is recently increasing within the scientific community due to the high bioreactivity of this pollutant (Seinfeld and Pandis, 1998).

Ammonia may be either wet- or dry deposited as a gas, or react with sulphuric, nitric and hydrochloric acids to form ammonium sulphate, bisulphate, nitrate, and chloride aerosols, thereby contributing to the increase of inorganic ambient particulate matter levels (Walker et al., 2004). These ammonium (NH_4^+) nitrate and sulphate aerosols contribute significantly to fine particle mass ($PM_{2.5}$) and have implications for human health (Brunekreef and Holgate, 2002). In addition, they alter global radiation budgets and limit atmospheric visibility (Clarisse et al., 2009; Horvath, 1992; Sutton et al., 1994). From a legislative perspective, they may be directly linked to the exceedance of the annual or daily limit values for PM_{10} in certain regions.

In urban environments, evidence suggests that vehicular traffic, malfunctioning sewage systems and human activity may have a major impact on ambient ammonia levels (Perrino et al., 2002; Meng et al., 2011), as correlations between NH_3 and traffic-related pollutants (NO_X and CO) have been found.

In Europe, urban ammonia is currently a topic of study for a limited number of research teams although to date no significant regulatory effort has been made to control emissions from motor vehicles. In January 2011, the government of Spain modified the current legislation about air quality (law 34/2007), adding a new regulation (R.D. 102/2011) which implements the obligation to measure ammonia levels in five rural background stations covering the country and in one traffic site in cities with more than 500000 inhabitants.

Secondary Organic Aerosols (SOA) accounts for the largest contribution to organic aerosols (OA) (Jimenez et al., 2009). There have been very few measurements that allow a direct estimation of the relative contribution of anthropogenic and biogenic precursors to the SOA formation and the uncertainties are still significant (Williams et al., 2007; Kleindienst et al., 2007). The formation of low-volatility compounds that make up SOA is governed by a complex series of reactions of involving a large number of organic species, so the experimental characterization and theoretical description of SOA formation presents a substantial challenge (Volkamer et al., 2006; Robinson et al., 2007 and Jimenez et al., 2009). The standard view is that SOA formation is dominated by a few classes of volatile organic compounds (VOCs) (mostly monoterpenes and aromatic compounds) but models usually underestimate the levels of SOA suggesting the importance of additional pathways of SOA formation not typically studied in experiments. Thus, the key concept underlying modern treatments of SOA is that it is composed predominantly of semivolatile organics, allowing for the description of SOA formation in terms of gas-particle partitioning.

1.4. AIR POLLUTION EFFECTS

The effects of PM on the atmosphere, climate, and public health are among the central topics in current environmental research. Aerosols particles scatter and absorb solar and terrestrial radiation, they are involved in the formation of clouds and precipitation as cloud condensation and ice nuclei, and they affect the abundance and distribution of atmospheric trace gases by heterogeneous chemical reactions and other multiphase processes (WBG, 2000). Moreover, airborne particles can cause or enhance respiratory, cardiovascular and allergic diseases (e.g. Pope et al., 1995; Dockery and Pope, 1996); play an important role in the spreading of biological organisms, reproductive materials, and pathogens (pollen, bacteria, spores, viruses, etc.); have a negative impact on construction materials (Tabasso and Marabelli, 1992; Alastuey, 1994); and reduce the visibility.

1.4.1. Air pollution and health

The effects of air pollution on public health are being felt worldwide. Pollutants, such as particulates (PM_x) and ozone, the latter primarily resulting from emissions of nitrogen oxides (NOx) and hydrocarbons/air toxins (HC or VOCs), destroy sensitive tissues (in people, animals and plants) and impair respiratory functions. Thus for example Bangkok has three times the rate of lung cancer as the rest of Thailand, this being mostly attributed to transport-related miasmas (Manins, 1997). The haze and filth from the diesel exhausts in Manila and Calcutta are so thick that it is frequently difficult to breathe (Manins, 1997; Lahiri et al., 2000; Krupnick et al., 2003). In Barcelona (Spain), Pérez et al. (2009) concluded that the annual mean health benefits of reducing the mean PM_{10} exposure estimated for the population in the study area (50 $\mu g\ m^{-3}$) to the annual mean value recommended by the World Health Organization (20 $\mu g\ m^{-3}$) were estimated to be 3500 fewer deaths (representing an average increase in life expectancy of 14 months), 1800 fewer hospitalizations for cardio-respiratory diseases, 5100 fewer cases of chronic bronchitis among adults, 31100 fewer cases of acute bronchitis among children, and 54000 fewer asthma attacks among children and adults. The mean total monetary benefits were estimated to be 6400 million euros per year if meeting WHO guideline. Reducing PM_{10} to comply with the current European Union regulatory annual mean level (40 µg m^{-3}) would yield approximately one third of these benefits.

A significant correspondence between exposure to atmospheric PM and several adverse effects on our health has been confirmed by many epidemiological studies (Dockery et al., 1993; Schwartz, 1994; Schwartz et al., 1996; Bascom et al., 1996; Dockery and Pope, 1996; Künzli et al., 2000; Wichmann, 2000; Pope et al., 2002; WHO, 2006; Pope et al., 2008). Effects on asthma are largely demonstrated for different type of aerosols components, including traffic PM, bioaerosols and other PM components (Kuenzli, 2012, McConnell et al., 2010; Castro-Giner et al., 2009; Salam et al., 2008). PM exposure can also lead to the development of obstructive airway diseases (Hogg et al., 2004). The link between the amount of respirable PM and the increase in human mortality is now well established, with an increase of 0.5% in daily mortality having been recorded for each 10µg m^{-3} increase in PM_{10} (Brunekreef and Holgate, 2002).

The effects caused by inhalation of PM depends on several properties, the main ones being size, chemical composition, solubility and exposure time to an atmosphere with high levels of PM. With regard to size, particles with a diameter less than 10 µm (PM_{10}) can enter the tracheobronchial region, they are called thoracic particles and are eliminated by cilia function. The particles with diameters between 0.1-2.5 µm can reach the alveolar region; they are called alveolar particles and cannot be eliminated, remaining chronically (Leopold et al., 1957). Particles less than 0.1 µm are too small to sediment during breath activity, however, they are deposited on alveolar walls by diffusion (Churg and Bauer, 1997). A small proportion of this deposited UFP may translocate lungs and reach the body organs (UBA, 2010). The chemical composition of the PM that will enter the lungs depends on the relative importance of major aerosol contributors, such as traffic, silicate dust, sea salt, sulphates and industrial metal condensates. Many of the particles in populated areas have their origin from road traffic and industrial sources. Some of the components in these particles, such as metals and PaHs are carcinogenic (Wu et al., 2009).

The biological mechanism underlying the adverse health effects is still unclear; an accepted hypothesis is that the oxidative damage originates from the surface of airborne particles (Squadrito et al., 2001; Bai et al., 2001; Greenwell et al., 2002). Oxidative damage is one of the important causes of fibrogenesis (Poli and Parola, 1996), and the reason for pulmonary illness such as chronic obstructive pulmonary disease, especially emphysema. Costa and Dreher (1997) have shown that bioavailable transition metal ions on the particle surface are a cause of oxidative stress. Pritchard et al. (1996) have reported that ionizable metals in airborne particles could catalyze oxidants, while indices of in vivo lung injury correspond to ionisable metal concentrations in airborne particles.

In addition to size and composition, the large surface area of ultrafine particles might also play an important role causing more severe health effects (Oberdörster et al., 2005; Stoeger et al., 2006). Only the surface area of particles deposited in the respiratory tract, hence the dose, may lead to health deterioration. That way, the determination of the lung deposited dose may be a better health-relevant value than actual airborne concentrations (Löndahl et al., 2007). Most of the processes in the human body environment take place via the particle surface, which is increasing significantly with decreasing particle size in the nanometer size range for the same amount of mass (Maynard et al., 2005; Fissan et al., 2007). The deposited dose will depend on different factors: exposure concentration, exposure duration, respiratory parameters, anatomy, sex and particle characteristic. The impact of ultrafine particles is remarkably different in each part of the lung. The most important parts of the lung are the tracheobronchial region and especially the alveolar region due to their enormous surface areas and the possibility to transfer particles into the blood stream and from thereon into all organs of the body (Kreyling et al., 2002). Toxicologists also discuss the possibility of particles deposited in the nose which can be transferred to the brain via the olfactory nerve (Oberdörster et al., 2004).

Associations have been found between long-term exposure to ambient air pollution and cardiovascular morbidity and mortality. Animal data suggest that ambient particulate matter (PM) may contribute to atherogenesis (Künzli et al., 2005).

1.5. URBAN AIR QUALITY

1.5.1. Air quality regulation

The objective of environmental legislations is to protect human health and the environment as a whole. For this, it is particularly important to defend air quality, combating emissions of air pollutants at sources by identifying and implementing the most effective emission reduction measures at local, national and European level. The current European policies target to two principal aims: ambient air quality and emission control.

As the result of European Union (EU) legislation, much progress has been made in tackling air pollutants such as sulphur dioxide, lead, nitrogen oxides, carbon monoxide and benzene. However, despite a reduction in some harmful emissions, air quality continues to cause problems. The European Comission (EC) has developed an extensive body of legislation which establishes health based standards and objectives for a number of pollutants in air. These standards and objectives are summarised in the table below (Table 1.2). These apply over differing periods of time because the observed health impacts associated with the various pollutants occur over different exposure times.

In short, the Council Directive 1996/62/EC on ambient air quality assessment and management recognizes the necessity of "*defining common objectives about air quality in European Community in order to avoid, prevent or reduce damaging effects on human health or on environment as a whole*". To that purpose, it was proposed to set limit and objective values or alert threshold for atmospheric pollutant concentrations and action plans when there is a risk of breaking requirements about air quality. The Council Directive 1999/30/EC, about limit values of certain pollutants in the air, establishes the obligation of controlling PM_{10}, SO_2, NO_X and Pb, defining limits for the concentrations of these pollutants. This Directive was transposed to the Spanish legislation by the 1073/2002 Real Decree, where two limits were proposed for the PM_{10} concentrations. These limits had to be achieved in 2005 and were called daily and annual limits. The annual limit requires the arithmetic average of PM_{10} concentrations measured during a year to be below 40 $\mu g\ m^{-3}$, while the daily limit asks for the 90.4 percentile of PM_{10} measured during a year to be below 50 $\mu g\ m^{-3}$. On the other hand, this Directive sets a limit value for annual average of Pb concentrations in air which is contained in PM_{10} in 500 ng m^{-3}. The second Daughter Directive 1999/30/EC included also target values for CO and benzene, while the third Daugther Directive 2002/3/EC added O_3. In addition, Directive 2004/107/EC indicates objective values for annual averages of PAH, Hg, As, Cd and Ni concentrations in PM_{10} to be reached in 2013, these values are 6, 5 and 20 ng m^{-3} for As, Cd and Ni, respectively. Finally, the New Directive 2008/50/CE of the European Parliament and the Council on ambient air quality and cleaner air in Europe (CAFE) unifies Directives 1996/62/EC and 1999/30/EC, as well as other texts in this field in order to improve administrative efficiency. This Directive sets the limit values of PM_{10} and Pb described in Directive 1999/30/EC as permanent. As innovative aspects, this Directive introduces a target value for $PM_{2.5}$ ($25\mu gm^{-3}$) concentrations which must become a limit value by 2015. In a second stage this Directive established an annual value of $20\mu g$ $PM_{2.5}$ m^{-3} that will be effective in 2020. The second stage will be revised by the Comission in the year 2013 with actualized information on effects on health and the environment, technical viability and the experience obtained with the target values in the Member States. Both Directives 2004/107/CE and 2008/50/CE are transposed to the Spanish legislation by Real Decree 102/2011.

The air quality Directive 2008/50/CE defines the $PM_{2.5}$ Average Exposure Indicator (AEI) for urban backgrounds, expressed in μg m^{-3} and based in measurements performed at urban backgrounds and agglomerations, as a three-calendar year running annual mean concentration averaged over all sampling points established. The AEI will be used to know if the exposure concentration obligation and the national exposure reduction target established by the Directive are met. The exposure concentration obligation establishes $20\mu gm^{-3}$ as the obligation value for the AEI to be met in 2015. The national exposure reduction target, to be met in 2020, depends on the initial ambient concentration, being between 0% when initial AEI are lower than $8.5\mu gm^{-3}$ and 20% for initial AEI between 18 and 22%. When levels are higher, additional measures should be taken until the levels reach to $18\mu gm^{-3}$.

Table 1.2. Current standard limits on air quality.

Pollutant	Concentration	Averaging period	Legal nature	Permitted exceedances per year
PM$_{10}$	50μg m^{-3}	24 hours	Limit value entered into force 1.1.2005**	35
	40μg m^{-3}	1 year	Limit value entered into force 1.1.2005**	n/a
PM$_{2.5}$	25μg m^{-3}*	1 year	Target value entered into force 1.1.2010. Limit value enters into force 1.1.2015	n/a
Exposure concentration obligation for AEI	20μg m^{-3}		Concentration obligation will enter into force in 1.1.2015	
Exposure reduction target for AEI	18μg m^{-3}		Targer value will enter into force in 1.1.2020	
Sulphur dioxide (SO_2)	350μg m^{-3}	1 hour	Limit value entered into force 1.1.2005	24
	125μg m^{-3}	24 hours	Limit value entered into force 1.1.2005	3
Nitrogen dioxide (NO_2)	200μg m^{-3}	1 hour	Limit value entered into force 1.1.2010***	18
	40μg m^{-3}	1 year	Limit values entered into force 1.1.2010***	n/a
Lead (Pb)	0.5μg m^{-3}	1 year	Limit value entered into force 1.1.2005	n/a
Carbon monoxide (CO)	10mg m^{-3}	Maximum daily 8 hour mean	Limit value entered into force 1.1.2005	n/a
Benzene	5mg m^{-3}	1 year	Limit value entered into force 1.1.2010	n/a
Ozone	120μg m^{-3}	Maximum daily 8 hour mean	Target value entered into force 1.1.2010	25 days averaged over 3 years
Arsenic (As)	6ng m^{-3}	1 year	Target value enters into force 31.12.2012****	n/a
Cadmium (Cd)	5ng m^{-3}	1 year	Target value enters into force 31.12.2012****	n/a
Nickel (Ni)	20ng m^{-3}	1 year	Target value enters into force 31.12.2012****	n/a
Polycyclic Aromatic Hydrocarbons (PAH)	1ng m^{-3} (expressed as concentration of Benzo(a)pyrene)	1 year	Target value enters into force 31.12.2012****	n/a

*Standard introduced by the Directive 2008/50/EC

**Under the Directive 2008/50/EC the Member State can apply for an extension until three years after the date of entry into force of the Directive 2008/50/EC in a specific zone. Request is subject to assessment by the Comission.

***Under the Directive 2008/50/EC the Member State can apply for an extension of up to five years in a specific zone. Request is subject to assessment by the European Comission.

***Under the Directive 2004/107/CE

1.5.2. Emissions regulation

According to the Air Quality Directive 2008/50/EC, emissions of harmful air pollutants should be avoided, prevented or reduced. Despite the high number of sources of PM in urban environments, only the direct exhaust emissions from road vehicles and industrial emissions are controlled so far.

Control on road traffic emissions is carried out by means of the EURO certification. The stages are typically referred to as Euro 1, Euro 2, Euro 3, Euro 4 and Euro 5 fuels for Light Duty Vehicle standards. Table 1.3 is a summary list of the standards, when they come into force, what they apply to, and which EU directives provide the definition of the standard.

Emissions of nitrogen oxides (NOx), total hydrocarbon (THC), non-methane hydrocarbons (NMTHC), carbon monoxide (CO) and particulate matter (PM) are regulated for most vehicle types, including cars, lorries, trains, tractors and similar machinery, although excluding seagoing ships and airplanes. Currently there are no standards for CO_2 emissions.

Table 1.3. European emission standards for exhaust emission from passenger cars (values are in g veh^{-1} km^{-1}).

Tier	**Date**	**CO**	**THC**	**NMHC**	**NOx**	**HC+NOx**	**PM**	**PN**
		g veh^{-1} km^{-1}						n/km^{-1}
DIESEL								
Euro 1 (1991/441/EC)	July 1992	2.72	-	-	-	0.97	0.14	
Euro 2 (1994/12/EC)	January 1996	1	-	-	-	0.7	0.08	
Euro 3 (1998/69/EC)	January 2000	0.64	-	-	0.5	0.56	0.05	
Euro 4 (1998/69/EC)	January 2005	0.5	-	-	0.25	0.3	0.025	
Euro 5 (2007/701/EC)	September 2009	0.5	-	-	0.18	0.23	0.005	$6.0x10^{11}$
Euro 6 (2007/701/EC)	September 2014	0.5	-	-	0.08	0.17	0.0025	$6.0x10^{11}$
PETROL (GASOLINE)								
Euro 1 (1991/441/EC)	July 1992	2.72	-	-	-	0.97	-	
Euro 2 (1994/12/EC)	January 1996	2.2	-	-	-	0.5	-	
Euro 3 (1998/69/EC)	January 2000	2.3	0.2	-	0.15	-	-	
Euro 4 (1998/69/EC)	January 2005	1	0.1	-	0.08	-	-	
Euro 5 (2007/701/EC)	September 2009	1	0.1	0.068	0.06	-	0.005*	
Euro 6 (2007/701/EC)	September 2014	1	0.1	0.068	0.06	-	0.005*	$6.0x10^{11}$

*Applies only to vehicles with direct injection engines

Regarding industrial emissions, the Directive 2008/1/EC (the IPPC Directive, Integrated Pollution Prevention and Control), which replaces Directive 1996/61/EC, defines the obligations that industrial and agricultural activities with a high pollution potential must comply. It establishes a procedure for authorising these activities and sets minimum requirements to be included in all permits, particularly in terms of pollutants released. The aim is to prevent or reduce pollution of the atmosphere, water and soil, as well as the quantities of waste arising from industrial and agricultural installations, to ensure a high level of environmental protection.

Shipping emissions are normally not reported in national inventories. The marine transport sector is especially polluting due to the use of low-quality residual fuels containing high amounts of sulphur and heavy metals (Eyring et al., 2005; Corbett and Koehler, 2003). Models estimate that SO_2, NO_x and $PM_{2.5}$ emissions from the maritime sector around Europe will increase by around 42%, 47% and 55% respectively by 2020 (Cofala et al., 2007). However, regulations governing shipping pollutants remain lax and primarily concerned only with the sulphur content of bunker fuel (2005/33/EC Directive for EU ports). The new EU low-sulphur Directive (Directive 1999/32/EC as amended by Directive 2005/33/EC) has now come into force and is aimed at controlling marine fuel emissions from vessels within EU ports. Article 4b of EU Directive 2005/33/EC requires that, with effect from 1 January 2010, Member States must take all necessary steps to ensure that ships berthed or anchored in European Community ports are not permitted to consume marine fuels with a sulphur content exceeding 0.1% by mass. This regulation applies to all vessels irrespective of flag, ship type, age or tonnage.

The Large Combustion Plant Directive (Directive 2001/80/EC) was introduced by the European Parliament and Council on the 23 October 2001. The Directive introduced measures to control the emissions to air of oxides of nitrogen (NOx), sulphur dioxide (SOx) and particulates from large combustion plants (i.e. plant with a rated thermal input of equal to or greater than 50 megawatt thermal).

There is a large number of PM sources which are difficult to control or without regulation, such as non-exhaust traffic emissions, diffusive emissions from constructions sites or domestic heating.

Diffusive emissions are particularly serious at construction sites, a source often hardly recognized but of main concern for urban air quality. These emissions are currenly unregulated, although some communities have published guidance for the prevention and control of PM emissions at construction sites:

- Stäubli, A., Kropf, R., 2004. Air pollution control at construction sites-construction guideline air. Environment in practice. Swiss Agency for the Environment, Forests and Landscape BUWAL, Bern.
- Regional Government of Styria, Austria. www. feinstaub.steiermark.at.2006.

- Best Practice Guidance. The control of dust and emissions from construction and demolition. Greater London Authority. November 2006.

-Best Practice Guidance. The control of dust emissions from demolition and construction. Government of Gibraltar. 2010.

1.5.3. Major causes of exceedances of limit values in urban areas across Europe

A marked decrease in the levels of PM_{10} has been reported from 1990 to 2009 in Europe (EEA, 2011), however, the impact of local sources in the urban scale can account for exceedances of current limit values.

In urban areas **road traffic** is the most important source of primary particles, with emissions from road transport arising from both exhaust and non exhaust sources (Viana et al., 2008). The most significant sources of non-exhaust PM are abrasion of brakes, tyres and components of motor vehicles, and the abrasion of the road surface itself (Amato et al., 2009b). A further non-exhaust source is the suspension or resuspension of previously deposited material from the road surface due to vehicle-induced turbulence, tyre shear and turbulent action of the wind (Querol et al., 1998b, Harrison et al., 2001; Querol et al., 2001; Querol et al., 2005; Charron and Harrison, 2005).

PM of exhaust origin tends to be in the fine ($PM_{2.5}$) fraction, whereas non-exhaust traffic-related processes tend to generate particles in the coarse ($PM_{2.5\text{-}10}$) fraction (APEG, 1999), although brake wear, for example, generates particles in both size ranges. As a result of the reduction in exhaust emissions, the relative importance of the non-exhaust emissions has increased. In a number of European cities exhaust and non-exhaust sources have been shown to contribute equally to total traffic-related emissions (Querol et al., 2004).

Particles from engines are mainly carbonaceous matter and show some trace elements as Cu, Ti, Zn and V (Schauer et al., 2006). Characteristic trace elements from traffic have changed much during the last decade. Thus, a rapid reduction of Pb and Br in urban air occurred in the late eighties, when the permissible Pb concentration in petrol was reduced (Lee et al., 1994).

Aerosol exhaust emissions can be emitted directly as particles (soot, carbonaceous aggregates formed during fuel combustion in the engine) (Fraser et al., 2003) or formed during the emission, dilution, mixing and cooling of the vehicle exhaust gases in ambient air (nucleation of H_2O-H_2SO_4 and some semi-volatile organic compounds) (Rodriguez et al., 2007; Casati et al., 2007; Jamriska et al., 2008; Robinson et al., 2007).

Diesel vehicles are an especially significant source of fine and ultrafine particles. In the last two decades diesel vehicles exceeded the emissions from gasoline vehicles by a factor of >10 in terms of mass concentration and > 10^5 times in terms of number concentration (Harris and Maricq, 2001). This difference has been reduced a lot by EURO 5 and EURO 6 vehicles, but diesel cars still may emit higher number of particles than gasoline cars (Ban-Weiss et al., 2009). However, gasoline vehicles are responsible for the formation of SOA in cities, contributing in about 80% (Bahreini et al., 2012). In Spain, the use of diesel vehicles is increasing and causing a descent in CO and CO_2 emissions, but an increase in the levels of suspended particles, mainly in the ones less than 1μm and in NO_2 (Pérez et al., 2008). Therefore, ratios between traffic-related gases are very different between cities depending on their vehicle fleet and it is difficult to establish a suitable control parameter.

Finally, road transport has also been established as the main source of non-agricultural ammonia emissions in urban areas followed by sewage systems (Fraser and Cass, 1998; Sutton et al., 2000) and garbage containers (Meng et al., 2011).

The impact of **industry emissions** (metallurgical processes, cement and ceramic production, etc) on air quality is still noticeable in some urban areas. They are responsible for high levels of trace metals, such as Cu, Pb, Cd and Ar, which can have important effects on human health (Barcan, 2002; Hedberg et al., 2005; Boyd et al., 2009). Industrial plumes of NOx and especially SO_2 have been reported to be responsible for enhanced levels of secondary inorganic aerosols (Fernández-Camacho et al., 2010). It has been also demonstrated that these emissions can cause extreme urban ozone diurnal variability (Zhang et al., 2004a).

Another potential, but hardly recognized source is the release of PM from **construction sites** or from quarries. In fact, this is an important source of PM in hot and predominantly dry areas, such as many cities around the Mediterranean, the Middle East, and in the southwest United States. They have a major local influence upon coarse particle concentrations (Deacon et al., 1997). Emission estimates are possible using equations presented by EPA (2006) or VDI (1999), but hardly any firm data is available on PM release from demolishing buildings or from blasting rocks. Additionally, large areas of land may be exposed to wind erosion, achieving high levels of $PM_{2.5\text{-}10}$ due to resuspension processes.

In spite of the relative impact of construction-demolition works emissions on PM_{10} and $PM_{2.5-10}$ levels, the contribution of this source is difficult to estimate, since the related trace metals content is close to typical soil dust or desert dust resuspended, and to the author's knowledge no detailed estimations or PM profiles of this source are currently available. Only few communities in Europe (e.g. Styria in Austria, Bern in Switzerland and London in UK) have published so far some guidance for the prevention and control of PM at construction sites.

To reduce levels of coarse fraction of PM emission, it is common to keep surfaces wet, but the fine material may still be available for later release (Winiwarter et al., 2009). Paved surfaces next to construction sites may contain 25 times the deposited PM mass (<10 mm) per square meter compared to residential or even traffic areas (Amato et al., 2009b). In estimating emissions it would be required to know to which extent dusty material is wetted, and to which extent it is removed from subsequent lifting into the atmosphere. In addition, vehicular on-road and off-road engines used in construction and demolition activities are much older than the ones used in road transport, they are an investment for many years, so they are likely to produce more harmful emissions.

In coastal urban areas, emissions from commercial **shipping** (passenger and cargo) may also constitute a relevant source of PM. Diesel engines on ocean going vessels are significant contributors to air pollution in many cities and ports (Lack et al., 2009, Pandolfi et al., 2010). Combustion of fuel oil in ports is an important source of SO_2 emissions with global, regional and local impacts (Derwent et al., 2005). According to global estimates, shipping emits between 0.9 and 1.7 million tons of total suspended particles (TSP) annually affecting coastal areas (Moldanová et al., 2009). Emissions from ship fuel-oil engines mainly consist of organic carbon (OC), ash, sulphate and inorganic constituents from combustion (V, Ni, Ca, Fe) (Moldanová et al., 2009). These emissions may account for 2-4% of the mean annual ambient air PM_{10} levels (25% primary particles and 75% secondary particles) and for 14% of the mean annual $PM_{2.5}$ in Mediterranean urban areas (Viana et al., 2009).

Biomass burning emissions, both controlled and from wildfires, have also become an important issue in air pollution as a source of particles in urban areas (Charlson et al., 1992; Fang et al., 1999; Simoneit, 2001). Source apportionment studies indicate relatively high contributions from the biomass burning source in winter in Central and Northern European areas (Szidat et al., 2006, 2007; Lanz et al., 2010), and also at six rural background sites on a west–east transect extending from the Atlantic (Azores) to mid-Europe (K-Puszta, Hungary), which were investigated during the CARBOSOL project (Puxbaum et al., 2007). Estimates of the contribution of domestic heating to $PM_{2.5}$ emissions vary from city to city (Denby et al., 2010): previous studies account for a contribution of up to 80% from wood combustion in Oslo (Larssen et al., 2006) while in Denmark wood burning represented around 47% of all Danish $PM_{2.5}$ emissions (Palmgren et al., 2005). Cities such as Helsinki have less significant contributions with wood burning estimated to account for just 24% of the local emissions (Kauhaniemi et al., 2008). However, in smaller cities in Finland and Denmark wood burning is estimated to be the dominating emission source. This percentage is expected to be much lower in south European cities where wood burning residential installations are infrequent (in Spain the number is estimated in less than 2000 installations in the entire country; www.avebiom.org) and mostly located in rural and suburban areas. On the other hand, the impact of agricultural fires and forest fires may be relevant in south Europe at regional and local scales (Alves et al., 2011; Kaskaoutis et al., 2011).

Domestic and residential emissions have generally a small contribution to PM levels in the urban scale, and they are even included in regional nitrate and sulphate contributions or in traffic contributions. In cities where coal is still used for domestic and residential heating and cooking, this source has been estimated to contribute by 2-13% to PM_{10} and by 5-19% to $PM_{2.5}$ (PNMCA, 2011).

Differences in the impact of the described sources are evident from region to region in Europe, so different national policies and control strategies might be needed to achieve a reduction of atmospheric aerosol levels on a continental scale, and thus standard control parameters must be always under review.

1.5.4. Differences in urban air quality between European regions

Sources and emission patterns may vary significantly across European cities. Furthemore, meteorology, photochemistry, and atmospheric processes governing air quality change in each region. Several studies have been carried out to synthesize and compare the characteristics and variability of the composition and physical properties of PM in different regions of Europe (Ruuskanen et al., 2001; Querol et al., 2004; Van Dinengen et al., 2004; Putaud et al., 2004; Götschi et al., 2005; Sillanpää et al, 2005; Puustinen et al., 2007; Rodriguez et al., 2005 and 2007; Jalava et al., 2007 and 2008). This section focuses on ultrafine particles (UFP) and carbonaceous compounds due to their reiterated reported association with human health.

Carbonaceous matter is a major constituent (up to 80%) of atmospheric aerosols in specific urban areas (Harrison et al., 2004; Querol et al., 2004; Yttri et al., 2009). They account for 30-60% of PM_1 levels in urban environments in southern Europe (Pérez et al., 2008) and are characterized by a complex mix of emission sources. They include primary elemental carbon (EC) from combustion of biomass and fossil fuels, primary and secondary organic carbon arising from combustion of biomass and fossil fuel, primary biological aerosol particles, which includes plant debris and fungal spores, and SOA from biogenic precursors (Ytrri et al., 2011). Black Carbon (BC) is defined as the carbonaceous material having intense black or dark colour and which absorbs visible light efficiently (Cachier, 1995). Often a smaller fraction of atmospheric BC is elemental carbon (EC) and most of it consists of highly polymerised organic material having rather low hydrogen to carbon and oxygen to carbon ratios (Cachier, 1995). However, the contribution of EC to BC can be highly increased close to its sources like, for instance, traffic. In northern European cities a number of recent studies have confirmed the importance of wood-burning emissions to ambient PM levels in wintertime (Glasius et al., 2008; Hedberg et al., 2006; Saarikoski et al., 2008; Szidat et al., 2009; Yttri et al., 2005, 2009). Scandinavia is a particularly interesting region with respect to natural sources of carbonaceous aerosols. Large forested areas, emitting vast amounts of VOCs during the long days of the Scandinavian summer, create a basis for biogenic secondary organic aerosols (BSOA) formation.

As discussed in previous sections, road traffic is frequently the main contributor to carbonaceous particles in populated urban areas in all European regions, with impact from exhaust and in a lower scale from non-exhaust sources. However, the way these emissions affect air pollution depends on several factors which vary across Europe and from city to city,

-Climatology: In dry south European areas, the non-exhaust emissions have been reported to contribute to PM levels more than in north Europe (Amato et al., 2011).

-Age of the vehicle fleet: The aging of the vehicle fleet will be responsible for enhanced emissions of some air pollutants like NH_3, as it has been reported that the highest average ammonia emission rates were observed for 10-year-old vehicles (Kean et al., 2009; Burgard et al., 2006).

-Dieselization of the vehicle fleet: The particulate emissions from diesel engines are in general higher than the emissions from spark ignition engines. Diesel engines have been found to emit usually a larger EC fraction (EC/OC>1) than gasoline engines

(EC/OC<1), although there is considerable variation between individual vehicles (Gillies and Gertler, 2000).

-Urban topography: The urban land use management influences the dispersion of traffic emissions, since the occurrence of narrow streets and reduced green areas prevent it. It is important to note that this land use also governed the way population is exposed to this source, as in many southern EU countries the urban population usually lives closer to traffic emissions than in the North of Europe.

-Mitigation strategies: National and local regulations on the use of private cars and investments on new clean technologies in public transport, as activities included in air quality plans, are a basic factor to control emissions. A lack of consciousness of Mediterranean cities in order to plan air quality programs promoting evaluation studies for air quality control has been reported (Umwelbundesamt, 2006).

In addition to the carbonaceous compounds mentioned so far, carbonate carbon (CC), or inorganic carbon are often not considered in many atmospheric chemistry studies. The reason for this may be its low contribution to fine particle mass in most studied areas (Sillanpää et al., 2005). Nevertheless, depending on the area of study or the meteorological conditions (e.g. type of soil, African dust events) CC concentrations may be significant. Recently, Querol et al. (2009) reported that across the Mediterranean basin and during the intrusion of air masses from North Africa, carbonate minerals may form up to 40% of the PM_{10} particle mass.

As discussed above, ultrafine particles in urban areas are mostly comprised of carbonaceous compounds from road traffic, but also of organic and inorganic secondary compounds (e.g. sulphate) This highlights the relevance of the favourable climatic conditions for secondary aerosol formation by photochemical processes in south-Europe, especially in summer, which can affect significantly the concentration and behaviour of these particles. 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., 2011). In addition, in the case of coastal cities, the significant SO_2 emissions from shipping may be transported towards the city with the sea breeze, enhancing the nucleation processes. Thus, the aerosol number size distribution is expected to vary widely between European regions. Asmi et al. (2011) accounted for a high seasonality of this parameter in the regional background of the Mediterranean area with highest levels in summer and spring, which was not observed in central Europe, this region presenting almost unimodal median distributions and relatively low variability. These authors, observed that the concentration distributions often show multiple modes, suggesting a combination of more polluted airmasses and cleaner air from the Arctic or Atlantic oceans in northern European areas, the number size distribution also showed a marked seasonality but lower levels than in the Mediterranean.

Therefore, strategies for urban particulate pollution control have to take into account specific regional characteristics including meteorology, proximity to the coast, soil cover, vehicle fleet and human habits and require correct information concerning aerosol sources. Although UFP and BC are not yet legislated in European countries, the growing interest on the behaviour and origin of these parameters in urban areas during the last years has resulted in he implementation of these measurements in numerous air quality monitoring networks across Europe. Several organisms and programs have shown the necessity of carrying out studies which allow increasing our knowledge about UFP concentrations in populated areas and their effects on human health, as shown in the examples below:

-The Second Position Paper on PM (EC, 2004), which showed the importance of studying the ultrafine particle sources: http://ec.europa.eu/environment/archives/cafe/pdf/working_groups/2nd_position_paper_pm.pdf.

-The Cost 633 Report (2009), which recommend including particle number as an additional parameter to the mass of $PM_{2.5}$: cost633.dmu.dk.

-The United Nations Economic Commission for Europe (UNECE) which has taken action to quantify and reduce the global black carbon emissions (ECE/EB.AIR/2007/7; UNECE Air Convention, 2011).

-The World Health Organization and the CAFE (Clean Air for Europe) program recognize that the most suitable parameter or parameters to control the particle concentration in urban environments is still unknown (WHO, 2006) and they show the importance of including paticle number and some chemical parameters as black carbon or organic matter in the air quality monitoring networks.

1.6. PRIOR STUDIES

The study of atmospheric aerosols in regional, rural and urban environments in the Western Mediterranean basin has been one of the main objectives of the Environmental Geochemistry research group at the Institute of Environmental Assessment and Water Research (IDAEA), through several PhD thesis and national and European research projects since 1995. These studies have been very important to understand the aerosol sources and processes under the typical conditions registered in Spain. The studies are described in this section and have been the starting point of the development of the present work.

The measurements of TSP and PM_{10} levels and speciation started in 1995 at the Teruel coal-fired power station, when the influence of the African dust on PM levels was first described and the impact of resuspension processes on coarse particle levels was reported (Querol et al. 1996, 1998a and 1998b).

Querol et al. (2001) showed hourly levels of $PM_{2.5}$ and PM_1 consistent with the daily cycle of gaseous pollutants emitted by traffic in Barcelona, concluding the necessity of abatement strategies against road traffic for aerosol control in large cities. In Rodriguez (2002), the impact of meteorology on PM levels was evaluated and a significant contribution of mineral dust in the urban environment, higher than that described in rural and industrial sites, was described. In addition, a first source apportionment study was carried out in Barcelona. Results in Viana (2003) revealed a high number of exceedances of daily Limit Value registered annually at urban monitoring sites, mostly caused by local sources, and the presence of local mineral pollution in big cities. The comparison between the PM_{10} and $PM_{2.5}$ chemical speciation results in southern-Europe with those obtained in central and northern European areas, described in Querol et al. (2004), concluded higher concentrations of mineral matter in southern Europe and highlighted a significant presence of secondary inorganic aerosols in intensively industrialised regions or heavily polluted urban areas. On the other hand, a complete characterization of levels of trace metals in different background stations in Spain was compiled in Querol et al., 2008, accounting for high NH_4NO_3 levels in Barcelona in comparison with other cities with a similar or higher traffic density.

In Escudero (2006) the suspended Particulate Matter and Wet Deposition Fluxes in regional background stations of the Iberian Peninsula were studied in the region of Barcelona, finding an important influence of african dust outbreaks and in Castillo

(2006), the impact of African outbreaks on PM levels and chemical speciation in the north-east of the Iberian was investigated.

In Pey (2007), the particle number concentration and size distributions were monitored for the first time in the Iberian Peninsula. This study concluded that the number concentration of UFP in urban areas was strongly dependent upon vehicle exhaust emissions, which may cause adverse health impacts. Moreover, urban Mediterranean environments were defined as favourable ambients for the production of nucleation-mode particles (<20 nm) by photochemical processes.

Pérez (2010) included a complete source apportionment analysis until 2007, introducing the PM_1 speciation in the urban environment of Barcelona. This work also extended the time series of particle number concentration and firstly described the diurnal cycle of BC in an urban background site in Barcelona. As a consequence, this parameter was proposed to be included in the air quality measurement networks as a road traffic tracer. On the other hand, Amato (2010) achieved the identification of road dust emissions by means of the Positive Matrix Factorizacion (PMF) receptor model carried out with the Multilinear Engine (ME) scripting, concluding the significant contribution of this source, which limits the effectiveness of regulations focused on exhaust emissions. The final aim of this study was to evaluate the effectiveness of street sweeping, washing and dust suppressants as mitigating measures to reduce road traffic emissions impact.

Furthermore, several studies have focused on the levels and behaviour of trace metals due to the reported effect of transition metal in human health risk (Moreno et al., 2006; 2007; 2010). The capacity of urban aerosols to contribute to the ability to generate hydroxyl radicals (OH) in vitro in $PM_{2.5}$ was evaluated in Barcelona by an international expert group counting on data from the Environmental Geochemistry group from IDAEA (Nawrot et al., 2009). They concluded that the levels of iron, zinc, lead and vanadium showed a marked correlation with OH formation and that transition metal may be the main responsibles for PM toxicity in the city.

Similar investigations to those in Barcelona have been carried out in other urban areas of Spain. In Madrid, the traffic impact (Artiñano et al., 2004; Karanasiou et al., 2011) and the secondary aerosol formation (Plaza et al., 2006) has motivated several studies. Sources and processes of urban aerosols were studied in detail in this city in Salvador (2003) and on-line OC+EC measurements have been performed in order to estimate the contribution of secondary organic carbon (Plaza et al., 2011). The impact of industrial activities has been studied with different purposes in Spain, such as studying the effects of emissions mitigation activities in Castellón (Minguillón, 2007; Minguillón et al., 2009), or the formation of ultrafine particles enhanced by industrial SO_2 emissions in Huelva (Fernández-Camacho et al., 2010; Fernández-Camacho, 2011). The interest on metal emissions from the industrial activity has led to perform several studies in the region of Andalucia (Sánchez de la Campa, 2010; de la Rosa, 2010; González, 2011). The chemical composition of particulate matter in the Basque country region was in-depth characterised by Inza (2010). The influence of the steel and metal industries on air quality has been detected in Gipuzkoa (Basque country) due to the high levels of Mn measured within the city (Lertxundi et al., 2010). The effect of the breeze and therefore the ship emissions impact on the urban air quality is another interesting item, which has been widely investigated in Santa Cruz de Tenerife (Rodríguez et al., 2008; González et al., 2011). In this city the impact of Saharan dust intrusions has also been widely studied (Alonso, 2007). In the region of Murcia, Negral (2010) interpreted the variability of PM_{10} and $PM_{2.5}$ levels in the environment and that of their majority, minority and trace components and identified the contributions of the air masses. Indoor and outdoor air quality health impacts are being investigated in Valencia (Esplugues et al, 2010). These examples highlight the extense investigation on urban environments carried out throughout Spain.

1.7. AIMS AND STRUCTURE OF THE THESIS

All the studies described above have contributed to extensively characterise PM in Barcelona and other Spanish regions. However, certain gaps were identified which need further investigation in the Mediterranean basin. Therefore, this thesis has been designed to cover the following aspects on urban air quality:

1. In spite of the well-known significant contribution of secondary particles to PM levels, there is not enough research on the factors controlling the variability of UFP in the Mediterranean area, including the formation of fresh particles. These studies are more widespread in northern Europe (Aalto et al., 1995; Olivares et al., 2007; Yttri et al., 2009) but can not be extrapolated to this region mainly for the different meteorological conditions.
2. The levels of secondary inorganic aerosols have been reported to be much higher in Barcelona than in other Spanish areas, regardless the intensity of the traffic impact in

each urban area (Querol et al., 2004 and 2008). The causes for these differences are still unclear.

3. The occurrence of fires in forested areas, agricultural fires, and domestic and residential biomass burning are likely to generate important emissions on a regional-scale around Barcelona, however, the impact of these emissions on PM levels in the city have not been characterised and quantified. Source apportionment studies indicate relatively high contributions of the biomass burning source in winter in Central and Northern European urban areas (Szidat et al., 2006, 2007; Lanz et al., 2010) but, to the author knowledge, dedicated source contribution studies are not available in southern Europe.
4. The investigation of air quality is encouraged by the potential negative impact on human health. Thus, it is very important to elucidate which pollution sources or PM properties in Barcelona are mostly implicated on aerosol toxicity.
5. Existing data on PM levels and composition have a coarse time resolution (24 hours to 1 hour), which limit the interpretation of aerosol sources and processes. Higher time-resolution data, especially on chemical speciation could be extremely valuable to understand primary and secondary aerosol processes as well as to gain deeper insights into their sources.

The identification of these knowledge gaps led to the continuation of the PM time series in an urban background site in Barcelona from 2008 to 2011, to extend the existing 2003-2007 series. Based on these data and focusing specifically on the Barcelona urban environment, the present thesis aims to achieve the following objectives:

1. To evaluate the impact of vehicular exhaust emissions on urban high time-resolved particle number (N) and Black Carbon (BC) concentrations.
2. To compare the relevance of UFP formation processes in Barcelona (as an urban environment representative of the Mediterranean region) with those from other urban environments in different European regions.
3. To identify the main aerosol sources and processes governing PMx levels in the city, by means of an intensive field campaign (DAURE), which involved the deployment of state-of-the-art instrumentation from 19 international teams.
4. To study the role of locally emitted NH_3 on the high contribution of secondary inorganic aerosols to PM mass in Barcelona.

5. To asses the impact of regional-scale biomass burning emissions on urban PMx levels in Barcelona by source apportionment analysis.
6. To evaluate the toxicological effects of urban atmospheric particles.

A methodology section summarizes the experimental and modelling techniques used to achieve the above objectives. Results are presented in form of five research articles adapted to include additional findings. The original articles are:

- Peculiarities in atmospheric particle number and size-resolved speciation in an urban area in the western Mediterranean: results from the DAURE campign.
- New considerations for PM, Black Carbon and particle number concentration for air quality monitoring across different European cities.
- Urban NH_3 levels and sources in a Mediterranean environment.
- Biomass burning contribution to urban aerosols in a coastal Mediterranean city.
- A multidisciplinary approach to characterise exposure risk and toxicology of PM_{10} and $PM_{2.5}$ in urban environments.

Finally, results are globally discussed and the main conclusions are presented. Annexes I and II present a list of participations in scientific meetings and related publications derived from results of this thesis.

CHAPTER 2: Methodology

1. METHODOLOGY

This section describes the methodology and instrumentation applied during the different monitoring periods and sampling campaigns which were carried out in the framework of this thesis.

1.1. STUDY AREA

The urban metropolitan area of the city of Barcelona has 1.63 million inhabitants (INE 2009), making it the second most populated city in Spain and the tenth within the European Union, with a density of 15990 hab km^{-2}. The city is located in the NE of the Iberian Peninsula, narrowly constricted between the Mediterranean and the Catalan Coastal Ranges (Figure 2.1) which help protect the city from the more severe continental weather conditions typical of inland Catalonia, but they also inhibit the advective effects of cleansing, Atlantic-derived air masses. Along its northern and southern margins the city is delimited by the Llobregat and Besòs river valleys that channel the winds and also contain major industrial activities such as metallurgy.

Due to the distinctive geography of the area, the transport and dispersion of atmospheric pollutants within Barcelona 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. This atmospheric dynamics and the geographic setting have the potential to produce high concentrations of locally derived pollutants within the city (Pérez et al., 2008).

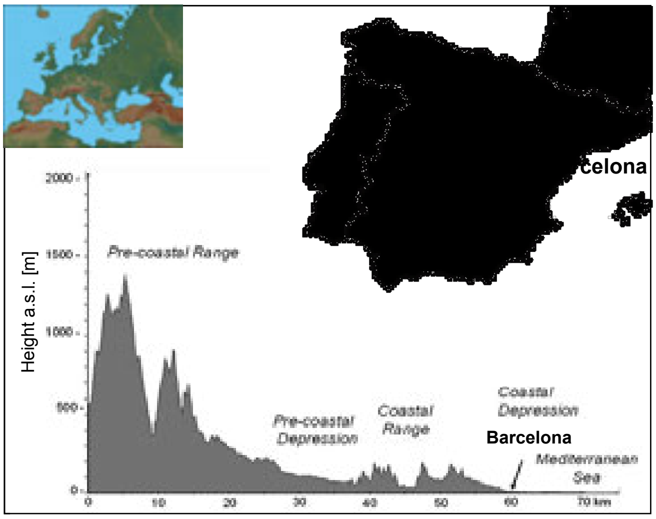

Figure 2.1. Location of the Barcelona Metropolitan Area in Catalonia, NE Spain (adapted from Pandolfi et al., 2012a)

Given the geographically confined nature of the city, the lack of central urban green spaces and the fact that Barcelona has one of the highest vehicle densities in Europe (6100 vehicles km^{-2}; according the statistics of Ajuntament de Barcelona, http://www.bcn.cat/estadistica/catala/index.htm), urban background levels are strongly contaminated by vehicle emissions. In addition to locally sourced air pollution, a further contribution to ambient PM concentrations in Barcelona is frequently made by the arrival of dusty air masses from the Sahara and Sahel desert regions of North Africa (Rodríguez et al., 2001; Moreno et al., 2006; Pérez et al., 2008; Pey et al., 2008). This contribution is estimated as directly adding around 1-2 µg m^{-3} to PM_{10} and 0.2-1 µg m^{-3} to $PM_{2.5}$ annual averages in the city (Escudero et al., 2007), as well as being responsible for 10-20 of the annual exceedances of the PM_{10} daily limit value (23-27% of total exceedances). However, most of the airborne mineral particles detected in Barcelona are anthropogenic in origin, resulting from resuspension from vehicular traffic, pavement abrasion, construction/demolition works and other human activities (Amato et al., 2009a).

A description of the mesoscale and local meteorological processes affecting Barcelona is provided in Pey et al. (2010) and Jorba et al. (2011). The general circulation of the atmosphere is governed by the influence of the Azores anticyclone, with a variable position depending on the season. In winter, the anticyclone is settled in southern latitudes, allowing low pressures above peninsular latitudes and thus favouring renewal of air masses. Since the end of spring until the beginning of autumn, the Azores anticyclone reachs its maximum intensity, avoiding the influence of low pressures from the Atlantic in the Mediterranean basin, this scenario favours the development of local and mesoescale circulations. During the diurnal period, as a consequence of high temperatures and the convergence of flows from sea to land, an area of relative low pressures is generated.

The air masses origin in the study area presents a typical seasonality as described in previous studies (Pey, 2007). The transport of air masses from the Atlantic is reported during the whole year, but with a major frequency during winter. On the other hand, the arrival of dusty air masses from Africa is more commonly produced in summer. On the other hand, advection episodes from central-Europe, from the southern Mediterranean basin and the anticyclonic scenarios are mostly reported during the autumn, winter and the beginning of spring. Finally, the local recirculation of polluted air masses is typical in summer.

Breeze patterns can also play an important role in the transport of pollutants within the city and from the urban to the rural sites. In Barcelona the sea breeze develops around 10:00 UTC, whereas levels of pollutants increase after 18:00 UTC when the mountain breeze starts bringing pollution in from the surrounding industrial valleys and the wider metropolis around the city centre. These temporal patterns are also of course reinforced by the increase in the boundary layer height during the central hours of the day (resulting in the dilution of pollutants) and its decrease starting at approximately 17-18h UTC.

Whereas air quality in Barcelona improved during the 1980-1990s, mainly due to reduced industrial emissions, lately the increasing traffic levels reversed this trend and Pérez et al. (2010) showed PM_1 mean annual levels increasing from 1999 to 2006, almost parallel to the progressive rise in road traffic flow and especially to the growth of the diesel fleet. However, in the last years, the influence of a favourable meteorology for pollutant dispersion and the economic crisis with the consequent reduction of vehicles at traffic rush-hours and the decrease of active industries, have reduced notably the PM levels, especially for trace compounds associated with industrial emissions (e.g. Cd, Cu, SO_4^{2-}) (Pérez, 2010).

As stated above, it is worth highlighting that the high population density of Barcelona accounts for the highest road traffic density of Europe. Barcelona is characterized by a high proportion of diesel cars (45%), motorbikes (29%), heavy duty vehicles (3%), and the use of a large proportion of private cars (40%) for the daily mobility of its inhabitants (Baldasano et al., 2007). 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.

2.2. AIR QUALITY MONITORING AND INTENSIVE CAMPAIGNS

2.2.1. Continuous measurements (2008-2010)

The main objective of these measurements was to continue with the characterization of PM levels and composition in the urban environment of Barcelona, which it has been ongoing within the group of Environmental Geochemistry since 2003 (and since 1999 in other sites of Barcelona). New instrumentations for a better understanding of the variability of submicronic and ultrafine particles have been introduced since, with an especial interest on the fine fraction due to their possible major influence on health, namely a WCPC TSI 3785 and a MAAP Thermo ESM Andersen.

At the beginning of this thesis (year 2008), the sampling station was located on the roof (two storeys) of the Institute of Earth Sciences “Jaume Almera” (IJA; 41º23’05’’N, 02º07’09’’E, 68 m.a.s.l) and exposed to road traffic emissions from the Diagonal Avenue (approximately 150 m distance), one of the largest avenues in the city. From 2009 onwards, the monitoring site was moved to a nearby location (about 450 m from IJA) in a public park in the north campus of the University of Barcelona (TG; 41º23’24.01"N 02º06’58.06"E, 80 m.a.s.l.). This site is less influenced by vehicular emissions from the Diagonal Avenue, at approximately a distance of 300 m.

By means of simultaneous measurements at both stations from February to December 2009, it was estimated that PM_{10} levels were 20% higher at IJA than at TG, while $PM_{2.5}$ and PM_1 concentrations were 16% higher at IJA. These differences between stations are necessary to be considered when analyzing the temporal variability in the city from 2008 to 2009 and for not attributing variations only to meteorological factors or emission changes. With regard to the chemical speciation, it is worth mentioning the high correlations (r^2=0.62-0.77) between TG and IJA levels of components directly related with traffic (EC, OC, Sb, Cu), industry (Cd, Co, Zn), fuel-oil combustion (V, Ni) and secondary inorganic factors (SO_4^{2-}, NO_3^-, NH_4^+), while for the mineral dust compounds (Rb, Al, Si, Ca, K, Mg, Ti, P) the correlations coefficients decrease significantly (r^2=0.1-0.3). This fact can be related with the significant contribution of construction works and traffic resuspension emissions immediately adjacent to the sampling points at IJA. On average, the mean mass of mineral matter concentration was 40% higher at IJA, the OM+EC was 30% higher, the sea salt 6% and the secondary inorganic compounds 15%.

- *Instrumentation*

From the beginning of the measurements, **on-line PM_{10}, $PM_{2.5}$ and PM_1 levels** were continuously monitored by PM optical counters (Grimm Labortechnik GmbH & Co. KG; models 1107, 1108 and a rack mounted environmental dust monitor model 180) (Figure 2.2) with 1-hour resolution. Models 1107 and 1108 were randomly used until the definitive installation of the model 180 in November 2008.

The model 1107 performs particulate size measurements by 90-degree laser light scattering. Air with multiple size passes through a flat laser beam produced by an ultra low maintenance laser diode. Due to the lack of a sample heater at the inlet even aerosols and semi volatile liquid particles can be identified. These counts from each precisely sized pulse channel are converted to mass using a particle density-based equation and the data is then converted to PM_{10}, $PM_{2.5}$ and PM_1. On the other hand, the model 1108 allows also obtaining particle counts in 15 channels and the mass distribution in 15 classes.

The model 180 has been designed for continuous, unattended automatic operation inside a shelter, container, building, etc. measuring continuously the momentary outdoor dust mass concentration of PM_{10}, $PM_{2.5}$ and PM_1. The main advantage of this version is the possibility to reduce maintenance to only an annual visit while assuring a very long and unattended operation.

For all models, a complete system consists of the TSP (total suspended particles) sampling head on top of the pipe, the attached temperature and humidity sensor, and the dehumidification section, and the laser detector.

Figure 2.2. Grimm monitor model 180.

Three high-volume samplers equipped with PM_{10}, $PM_{2.5}$ and PM_1 inlets (DIGITEL, MCV; 30 m^3 h^{-1}; Figure 2.3), provided **24 hours PM_{10}, $PM_{2.5}$ and PM_1 samples collected on quartz micro-fibre filters** (Schleicher and Schuell and Munktell filters). PM mass concentrations on the filters were determined by standard gravimetric procedures with an uncertainty of 1.5 µg m^{-3} (Viana et al., 2006). The gravimetric data obtained were used to correct the PM_{10}, $PM_{2.5}$ and PM_1 measurements obtained with the optical counters, following the specifications of the “Guide for Member States for PM_{10} monitoring and intercomparison with the reference method” (EC, 2002).

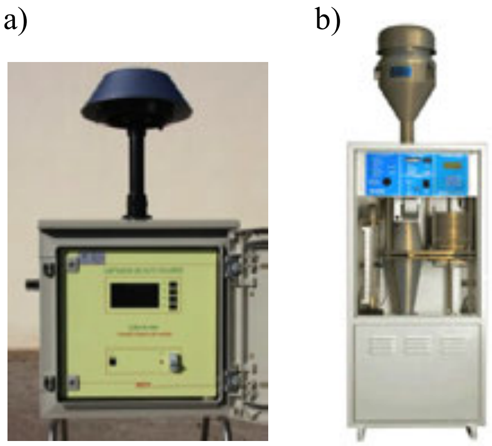

Figure 2.3. High-volume samplers: a) Manual MCV and b) Secuential Digitel.

A total amount of 376 PM_{10}, 320 $PM_{2.5}$ and 325 PM_1 samples were collected from 2008 to 2010 without considering here those samples from the intensive field campaign DAURE, described in the following section.

From January 2009, levels of **Black Carbon (BC) concentrations** were continuously monitored by a multi-angle absorption photometer (MAAP, Thermo ESM Andersen Instruments) with a PM_{10} inlet (Figure 2.4), operating on a 1-min time resolution. The monitor determines the absorption properties of light absorbing aerosols suspended in the ambient atmosphere. The basic principle is based on light attenuation by absorption, scattering and reflection of particles accumulated on a moving filter tape. The instrument measures absorbance (m^{-1}) from particles deposited on the filter using measurements of both transmittance and reflectance at different angles. The absorbance is converted to the mass concentration of BC (gm^{-3}) using a fixed mass absorption cross section at 637 nm (Müller et al., 2011) of 6.6 m^2 g^{-1} recommended by the manufacturer. Nevertheless, experimental results showed an average absorption cross section of 9.2 m^2 g^{-1} in Barcelona. These 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). This experimental conversion factor ($9.2m^2g^{-1}$) was used in this study to convert absorbance to mass concentration of BC.

Figure 2.4. MAAP for BC measurements

The **total particle number concentrations** in the size range between 5 and 1000 nm was obtained by means of a water-based particle counter (WCPC TSI 731 3785; Figure 2.5), with a 5-min time resolution from February 2009 onwards. The WCPC uses a laser and optical detector to detect the particles, passing the sampled flow through a viewing volume illuminated by a laser. The instrument relies on a condensation technique to deposit a working fluid on the particles to grow or “amplify” their size to a value that can be detected readily with a conventional optical system. The aerosol enters the sample inlet and immediately enters a region surrounded with wetted media. This results in a supersaturated condition along the radius of the flow stream.

Particles in the flow stream act as nuclei for condensation. Water continues to condense on the particles as they pass up the growth tube and the enlarged particles are then detected by the optical detector.

Figure 2.5. WCPC TSI 3785 for measurements of number particle concentrations.

Real time monitors for gaseous pollutants for NO, NO_2 (SIR S-5012), CO (Ecotech EC 9830), O_3 (SIR S-5014) and SO_2 (Thermo Scientific Model 43C), were operated on a 1-minute time resolution throughout the entire measurement period. Monitors were supplied by the Department of Environment of the Autonomous Government of Catalonia.

Additionally, a meteorological station located on the roof of the Faculty of Physics from the University of Barcelona (at about 100m from IJA and 400m from TG) provided continuous measurement of wind speed and direction, temperature, relative humidity, precipitation and solar radiation.

- *Chemical analysis*

Once the gravimetric determination of the PM mass concentration was performed, the PM_{10}, $PM_{2.5}$ and PM_1 filter samples were treated and analyzed for the complete characterization of the chemical composition to identify emission sources affecting the monitoring site. To this end, one quarter of each filter was acid digested ($HF:HNO_3:HClO_4$), kept at 90°C in a Teflon reactor during 6 h, driven to dryness and re-dissolved with HNO_3 to make up a volume of 50 ml with water, to be analysed using **Inductively Coupled Plasma Atomic Emission Spectrometry for the determination of the major elements** (ICP-AES: IRIS Advantage TJA Solutions, THERMO) and **Mass Spectrometry for the trace elements** (ICP-MS: X Series II, THERMO). To assure the quality of the analytical procedure a small amount (10 mg) of the NIST-1633b (fly ash) reference material loaded on a 1/4 quartz micro-fibre filter was also analysed. Within each digestion, the *Standard Reference Material® 1633b Coal Fly Ash* was used to calculate the recovery yield of elements analysed by ICP-MS and ICP-AES, according to the following equation:

$$R_j = \frac{x_j}{x_{cj}} \cdot 100 \qquad (1)$$

where R_j is the recovery yield (expressed in %) (Table 2.1), x_j is the fraction mass of jth analyte to the total digested mass and x_{cj} is the certified fraction mass of jth analyte to the total digested mass.

Table 2.1. Elemental recovery yield after Standard Reference Material digestion. *only indicative (non-certified values).

Element	Certified value (µg g^{-1})	SD (µg g^{-1})	Mean value found (µg g^{-1})	SD (µg g^{-1})	R_j
Al	150500	2700	140182	2164	93%
Ca	15100	600	14235	896	94%
Fe	77800	2300	69770	4569	90%
Mg	4820	80	4474	96	93%
Na	2010	30	2592	205	129%
S	2075	11	867	660	42%
K	19500	300	18116	117	93%
Sc	41.0*		37.8	2.0	92%
Ti	7910.0	140	7490.7	385.9	95%
V	295.7	3.6	280.5	36.2	95%
Cr	198.2	4.7	182.8	30.7	92%
Mn	131.8	1.7	121.6	18.0	92%
Co	50.0*		44.0	5.2	88%
Ni	120.6	1.8	95.8	22.1	79%
Cu	112.8	2.6	108.2	13.3	96%
Zn	210.0*		208.5	18.6	99%
As	136.2	2.6	125.9	5.2	92%
Se	10.3	0.17	11.8	0.9	115%
Rb	140.0*		117.7	8.3	84%
Sr	1041.0	14	958.9	50.9	92%
Cd	0.8	0.006	0.8	0.2	102%
Sb	6.0		5.8	2.2	97%
Cs	11.0		9.4	1.3	86%
Ba	709.0	27	656.3	40.1	93%
La	94.0*		67.0	9.0	71%
Ce	190.0*		176.3	5.2	93%
Hf	6.8*		7.6	2.5	112%
W	5.6*		13.5	7.0	241%
Tl	5.9*		5.3	0.8	90%
Pb	68.2	1.1	62.8	2.4	92%
Th	25.7	1.3	23.7	0.7	92%
U	8.8	0.36	7.9	0.8	90%

One remaining quarter of each filter was leached in 30ml of bi-distilled water for the extraction of **water-soluble ions** and subsequent analysis by **ion chromatography (IC-HPLC)** for sulphate, nitrate and chloride and by specific electrode for ammonium. A section of 1.5 cm^2 was used for the determination of **OC and EC by a thermal-optical**

transmission technique (Birch and Cary, 1996) using a Sunset Laboratory OCEC Analyser with the EUSAAR 2 temperature program.

In all cases laboratory blank concentrations were subtracted for the determinations of final concentrations in ambient air.

2.2.2. DAURE intensive campaign

DAURE (Determination of the sources of atmospheric Aerosols in Urban and Rural Environments in the western mediterranean) was an international field campaign aimed at characterizing the sources of fine aerosols in the Barcelona region, with particular attention to carbonaceus aerosol. This intensive campaign was carried out in addition to the ongoing PM characterization between 2008-2011 at the TG station.

The DAURE campaign took place during winter (February–March 2009) and summer (July 2009) at an urban site (previously identified as TG) and a regional background site (Montseny, 41º56'N 02º21'E, 720 m a.s.l., NE Spain a Supersite of the EUSAAR network). The results discussed in this thesis are focused on the data obtained for the urban site in winter, the period during which a more extensive on-line and off-line data set was obtained. The large participation of different international expert groups on atmospheric pollution within DAURE allowed to count on data from widespread in situ techniques as well as state-of-the-art methods. These state-of-the-art methods (see description below) have been used more frequently in central Europe (Lanz et al., 2010; Mohr et al., 2011) and only rarely in the Mediterranean region. Some premises make experts believe that the results from Central Europe (dominance of biogenic and biomass burning in the organic aerosol) may not be directly extrapolated to the Mediterranean, and this campaign represented an opportunity to evaluate this hypothesis.

-Instrumentation

Table 2.2 reports the participant and collaborating research groups involved in the DAURE sampling campaign in the urban background site and the instruments used in the framework of this study. During the campaign, meteorological stations providing wind speed and direction data, temperature, relative humidity, precipitation and solar radiation were also installed at TG.

Table 2.2. Summary of the participating groups and instrumentation deployed during the DAURE campaign and employed for the aims of this study.

Participant groups	***Country***	***Technique***	***Parameter***	***Notes***
IDAEA-CSIC-BCN (National Research Council)	Spain	Optical counter	1h PM_{10}, $PM_{2.5}$, PM_1	PM levels corrected with gravimetric measurements
		High volume samplers	12 h quartz micro-fibre filters of PM_{10}, $PM_{2,5}$ and PM_1	A total amount of 58 PM_{10}, 64 $PM_{2.5}$ and 64 PM_1 were collected and chemically characterised.
		MAAP	Black Carbon mass	
		CPC	particle number	Size range: 5-1000 nm
		Meteo data	Wind speed and direction, T, RH, precipitation, solar radiation	Data from a meteorological tower at 10 m high
PSI (Paul Sherrer Institute)	Switzerland	HR-ToF-AMS	Organics, NO_3^-, SO_4^{2-}, NH_4^+, Cl^-	Sub-micron aerosol mass loading measurements
		SMPS	Aerosol size concentration and distribution	Aerosol size range: 9-615 nm; 116 bins
		Rotating Drum Impactor	PM_1, $PM_{1-2.5}$, $PM_{2.5-10}$	Hourly-resolved elemental aerosol composition
CREAF (Centre for Ecological Research and Forestry Applications)	Spain	PTR-MS	Real time VOCs measurements	
CIEMAT (Centre for Energy, Environment and Technology Research)	Spain	R&P8400N particulate nitrate analyser	Nitrate concentration	

In addition to the groups directly measuring and sampling at the urban background site, it was essential the involvement of the following groups for the organization and implementation of the campaign:

-University of Colorado-Boulder, USA (PI Jose Luis Jimenez),

-Atmospheric Sciences Dept. at the Centre for Ecology and Hydrology, Edinburg, Scotland, UK (PI Eiko Nemitz),

- Ion Chemistry Group, University of Innsbruck, Austria (PI Armin Hansel),

- BSC: Barcelona Supercomputing Centre, Spain (PI Jose Maria Baldasano),

- Department of Signal Theory and Communications (TSC) (Lidar experts), Barcelona, Spain (PI Michaël Sicard),

- Atmospheric Physics Group of the University of Barcelona, Spain: Aerosol optical characterization from columnar radiometric measurements, Cimel sunphotometer, spectroradiometers and meteorological instruments (PI Jeroni Lorente),

- Aerodyne Research, Boston, USA (PI John Jayne).

The instruments deployed exclusively for the DAURE campaign period at the TG station, in addition to the methods described for the continuos measurements, were:

- One **Aerodyne high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS)** (Figure 2.6), operating at a 2.5-minute time resolution. The HR-ToF-AMS uses the same aerosol sampling, sizing, vaporization and ionization schemes as those of the Q-AMS (Jayne et al., 2000; Jimenez et al., 2003) and the Compact- ToF-AMS (Drewnick et al., 2005). A detailed description of this instrument is given in DeCarlo et al. (2006). It was used throughout the complete campaign in order to determine on-line levels in PM_1 of organic aerosols, NO_3^-, SO_4^{2-}, NH_4^+ and Cl^-.

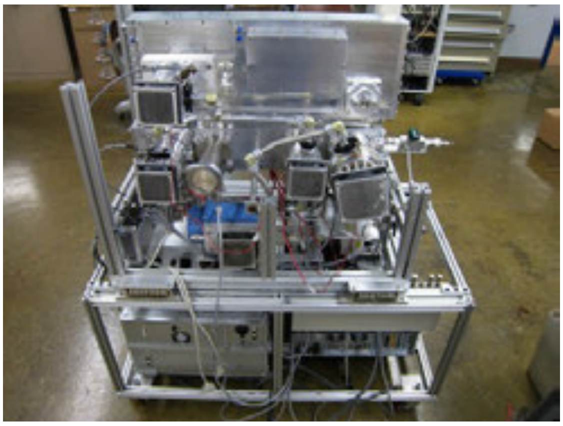

Figure 2.6. HR-ToF-AMS for online speciation of the non refractory fraction of PM.

- One **scanning mobility particle sizers (SMPS)** consisting of a neutralizer (85Kr-source), a DMA and a CPC (TSI model 3022A), operating on a 5-minute time resolution (Figure 2.7). This equipment provided a complete size distribution of the particle number between 13 and 650 nm. Note that before particles enter the DMA, a volume of sampling air was dried with a system operated with silica gel, after which a zero filter was installed. When this air is mixed with the sampled air, the dilution system reduces the humidity of the ambient air, so that measurements were carried out on dry aerosol particles (relatively humidity less than 20%).

Figure 2.7. SMPS for measuring on-line segregated number aerosol concentrations.

- One **three-stage rotating drum impactor (RDI)** (Figure 2.8). The RDI divides the aerosol particles into the following sizes: 10-2.5 µm, 2.5-1 µm and 1-approx. 0.1 µm with a sample flow of 16.6 l min^{-1}. Aerosols deposit on a 6-µm greased polypropylene film and are subsequently analyzed by synchrotron radiation X-Ray fluorescence spectrometry (SR-XRF, see Bukowiecki et al., 2009 for details) to obtain the concentration of 26 major and trace elements on an hourly basis.

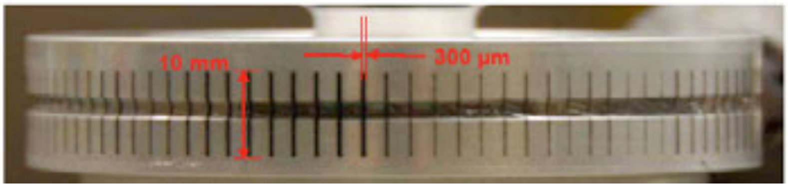

Figure 2.8. RDI sampling drum: a notched aluminum wheel, coated with a 6-µm PP film, used for sampling and subsequent SR-XRF-analysis

A **proton transfer reaction-mass spectrometer** (**PTR-MS** from Ionicon Analytik Innsbruck, Austria) providing data on Volatile Organic Compounds with a resolution of 7-8 minutes (Figure 2.9). The PTR-MS method has been described in detail in numerous publications (Hansel et al., 1995; Lindinger et al., 1998).

Figure 2.9. PTR-MS for on-line measurements of VOCs.

- *Chemical analysis*

The chemical analysis performed on the 58 PM_{10}, 64 $PM_{2.5}$ and 64 PM_1 quartz micro-fibre filter collected during this campaign was very similar to that employed during the continuous measurements, with some key differences: (1) the sampling time resolution was higher, obtaining the chemical composition for 12-hour periods every day (from 9 to 21 and from 21 to 9 h UTC), (2) leachates were also analysed by ICP-AES in search for the soluble fraction of major compounds and (3) one quarter of each $PM_{2.5}$ filter was used for the determination of organic compounds. For the objectives of this study, an important determination regarding the organic fraction speciation was the analysis of monosaccharide anhydrides, namely levoglucosan, mannosan, and galactosan.

The **monosaccharide anhydrides** were determined using a **high-performance anion-exchange chromatograph with a quadrupole mass spectrometer** (HPAEC-MS). The description of the method has been presented in detail by Saarnio et al. (2010a). In short, a 1-cm^2 punch was taken from each quartz filter sample. The analytes were extracted from the filter pieces with 2.5 ml of deionized water containing 120 ng ml^{-1} of internal standard (carbon-13-labeled levoglucosan) by a short manual shaking followed by 15 min of gentle rotation. The extract was filtered before injection to the analysis (sample loop volume of 50 µl). The analyses were conducted with a Dionex ICS-3000 system equipped with a Dionex CarboPac™ PA10 guard column (2 mm i.d. × 50 mm length) and a Dionex CarboPac™ PA10 analytical column (2 mm i.d. × 250 mm length), a 2-mm ASRS® 300 suppressor, a CR-ATC anion trap column, and an EGC II KOH eluent generator. The analysis run was isocratic (2 mM KOH) lasting eight minutes per sample. The used ionization technique was electrospray ionization. The molecular ions of monosaccharide anhydrides were determined with a Dionex MSQ™ mass spectrometer with m/z 161 and the internal standard with m/z 167.

Concentrations of monosaccharide anhydrides were below the detection limit (2 ng m^{-3} for Levoglucosan and 0.9 ng m^{-3} for Mannosan and Galactosan) for more than 96% of days during the summer period of the DAURE campaign. Thus, results and discussion on this item will focus on the winter period.

2.2.3. Urban NH_3 levels and sources determination (2010-2011)

Because of the high levels of secondary inorganic aerosols registered in Barcelona, and as a response to the recent regulation of NH_3 measurements in urban areas in Spain, specific campaigns for the determination of levels and behaviour of this pollutant were devised. In order to determine the spatial distribution of ammonia concentrations in the Barcelona metropolitan area, 58 locations (34 urban background and 24 urban traffic sites) were selected for summer sampling betweem 07/07/2010 and 21/07/2010. During this period, a regional background site was also selected for comparisons (Montseny; 41º56'N 02º21'E, 720 m.a.s.l). For the winter period (17/01/2011-28/01/2011), 56 of the above locations (32 urban background and 24 urban traffic sites) were used (Figure 2.10). The passive samplers used (see below) were located on street lights, traffic signs, traffic lights, balconies, etc., at approximately 2-2.5m from ground level being exposed for 12-14 days each. In order to check the repeatability of the method, replicate samples were collected in three of the selected sites in each period.

Figure 2.10. Selected sampling points for the summer (a) and the winter (b) periods. The historic city centre is highlighted with a black square.

To complement the information obtained from the main sampling campaign described above, additional source-specific campaigns were carried out to better identify potential NH_3 sources. Samplers were deployed in the city aiming to characterise four different sources: traffic, garbage containers, the sewage system and the accumulation of garbage outside a central open-air market. With this aim the following measurement schemes were devised and applied:

a) From 17/11/2011 to 04/12/2011, 8 samplers were placed perpendicularly to the Diagonal Avenue (traffic density of 132000 vehicles day^{-1}), along a street with a low number of vehicles per day (traffic density of 15000 vehicles day^{-1}), in order to observe if levels decreased progressively with increasing distance to the avenue, and trying to estimate the contribution of road traffic to the NH_3 concentrations.

b) The impact of garbage containers was studied by two different approaches: (1) levels obtained from the summer and winter campaigns were averaged as a function of city districts and compared with the number of garbage containers in each district and (2) from 19/07/2011 to 26/07/2011 samplers were located in the vicinity of garbage containers to investigate a potential increase in the levels as measures were taken closer to this source.

c) The sewage system contribution to total NH_3 levels was also studied from 17/11/2011 to 04/12/2011. A total amount of 20 samplers was deployed throughout the city with the aim to capture the contribution from sewers emissions to urban NH_3 levels closest to the sea (with higher flows-rates) and sewers closest to the mountain (with lower flow-rates). The distinction between both areas of the city is motivated by the sewage system design which is built on a slope with all the sewer pipes joining close to the sea, reaching there the maximum flow. The samplers were placed attending to three conditions: (1) the sampling points were at least 50 m away from traffic and waste containers emissions, (2) samplers were deployed two meters immediately above sewers, and (3) whenever possible the sampling points were located in narrow streets with scarce ventilation.

d) The potential impact of an open-air market located in the city centre was also investigated by a specific sampling campaign from 19/07/2011 to 26/07/2011. In this campaign, 13 passive samplers were located at different distances to the market, selecting points characterised by different dispersion and ventilation conditions.

Additionally, from the start of the monitoring period until the end of 2011, a routine sampling strategy of one sample per week was carried out at an urban background site (Palau Reial; 41º23’13.08’’N 02º06’50.11’’E), which is influenced by vehicular emissions from the Diagonal Avenue, located at approximately a distance of 300 m. In this way, concentrations obtained at this site could be used as reference values for comparison during all the sampling campaigns.

-Instrumentation

For the study of the NH_3 levels in Barcelona, a high sensitivity **passive sampler** (**CEH ALPHA**: Adapted Low-cost High Absorption) (Tang et al., 2001) was used. In short, samplers are made up of circular polyethylene vial with one open end (Figure 2.11). An internal ridge supports a filter, which is coated with a solution of phosphorous acid in methanol, which serves to capture the ammonia, and is held in place with a polyethylene ring. The open end is capped with a polyethylene cap with a hole punched out in the centre, which holds in place a PTFE membrane (27 mm diameter) allowing gaseous ammonia to diffuse through. The end of the sampler is sealed with a top protective cap, which is removed prior to exposure. Exposed filters were then stored at 4ºC until analysis. Then they were leached in 3 ml of milli-q water to determine ammonium ion concentrations by ion selective electrode.

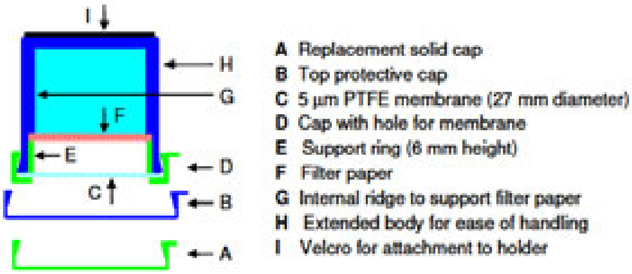

Figure 2.11. Diagram of passive ALPHA sampler for NH_3 measurements (Tang et al., 2001).

The self consistency of the method was validated by carrying out simultaneous field samplings (8 samplers plus 2 blanks) of different time durations: the first sampler was exposed during three days and the rest of them were systematically exposed during 24 additional hours than the previous one. Results showed that concentrations were stable from day 6 onwards, so this number of days was considered the minimum to obtain representative levels under the sampling conditions in Barcelona.

In order to check the reliability of the ALPHA samplers, results were compared with on-line measurements from an on-line AiRRmonia instrument (httl: www.mechatronics.nl) (Figure 2.12) during a two months campaign carried out in two urban background monitoring sites in Barcelona. Results on the daily evolution of NH_3 at both sites are described in detail in Pandolfi et al. (2012b).

The AiRRmonia has been intercompared with other ten instruments for the measurement of ambient concentrations of atmospheric ammonia gas (NH_3), based on seven different measurement methods, showing a good performance (Bobrutzki et al., 2010). The instrument uses a membrane to select the ammonia from the airflow into de-mineralised water flow and it determines NH_3 levels based on electric conductivity changes induced by ammonium concentrations in the solution. The airflow of the instrument is about 1 l min^{-1}.

Figure 2.12. AiRRmonia

2.2.4. Air pollution and health

-Urban aerosols bioreactivity evaluation (2008-2009)

This campaign aimed to evaluate the Reactive Oxygen species (ROS)-generating capacity of urban aerosols in Barcelona. These species can cause oxidative stress through the oxidation of biomolecules, leading to cellular damage that may become irreversible and cause cell death. This study was performed with samples collected at the IJA sampling site.

Instrumentation

This study uses PM chemical data from measurements carried out during two whole years, from January 2008 to December 2009. Until April 2009 three high-volume samplers equipped with PM_{10}, $PM_{2.5}$ and PM_1 inlets (MCV; 30 m^3 h^{-1}) were deployed at the IJA site, providing 24-hour samples collected on 150 mm quartz micro-fibre filters (*Munktell*) twice a week. From this date on, only PM_{10} samples were available until the end of the study period with the same frequency.

Collections for toxicological characterization were performed from October 2008 to December 2009 using a **High Volume Cascade Impactor (HVCI)** (Rupprecht and Pataschnick, USA), first described by Demokritou et al. (2002). It consisted of a 3-stage metal cylindrical head, mounted on a heavy duty tripod and a pump. Air was drawn through the head at 900 l min^{-1}. The HVCI operated as a 3-stage-polyurenthane foam (PUF) collection head, with the two lower stages dividing the PM_{10} into $PM_{2.5-10}$ and $PM_{0.1-2.5}$. PUF foam substrates were weighed pre- and post-sampling on an analytical balance, following the protocole explained by Moreno et al. (2004). To minimise chemical alteration of the particles, the only medium used in the extraction procedure was mili-q water. The samples were then agitated in a Vortex Geie II for an hour, followed by 2 minutes sonication. The substrates were afterwards spread out as much as possible without being damaged whilst remaining submerged, taken out of the tube and stored in a freezer. Finally, the sample was then freeze-dried to obtain particles in a solid state once again. The main limitation of this extraction procedure is that the organic fraction can not be extracted from the PUF using mili-q water.

Chemical analysis

The quartz micro-fibre filters were analysed as described in the section 2.2.1 for the characterization of the inorganic compounds.

For the toxicological tests, quartz filters were also analysed in search for polycyclic aromatic hydrocarbons (PAH) concentrations. To this end, 1/8 part of the filter sample was used. The determination method was widely described in van Drooge et al., 2009a. In brief, filter samples were spiked with surrogate standards, anthracene-D, benz[a]anthracene-D, benzo[k]fluoranthene-D and benzo[ghi]perylene-D, and extracted in a mixture of hexane and dichloromethane (DCM) (3 x 5mL; 9:1 v/v; Merck, Germany) and cleaned-up on 1g aluminium oxide (Merck, Germany) column chromatography and further concentrated to 25 µl isoocthane containing 100 ng pyrene-D as internal standard. Then, the following PAH: phenanthrene (Phe), anathranece (An), fluoranthene (Fla), pyrene (Pyr), benzo[a]anthracene (BaA) chrysene+thriphenylene (Chr+Tri), benzo[b+j]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[e]pyrene (BeP), benzo[a]pyrene (BaP), indeno[123cd]pyrene (IP), dibenzo[a]anthracene (DBA)), benzo[ghi]perylene (BgP), were analyzed by **gas-chromatography coupled to mass-spectometry** (GC-MS, Thermo Trace) on a 60 m fused capillary column (HP-5MS, 0,25 mm x 0.25 µm film thickness). Quantification was performed by calculating the concentrations of the analytes with the external standard calibration curve. Calculated concentrations were corrected for the recoveries of the above mentioned surrogate standards.

Toxicological characterization

The toxicity of the PAH analysed in the filter samples was determined as the calculated toxicity equivalent of benzo[a]pyrene (BaPteq) after application of EPA toxicity factors (Schoeny and Poirier, 1993).

To carry out a bioreactivity characterization, a selection of 20 $PM_{2.5-10}$ and 20 $PM_{0.1-2.5}$ simultaneously collected PUF samples was made corresponding to different meteorological scenarios in the studied site, including Atlantic advection, north African Saharan intrusion and local pollutant accumulation under stagnant conditions. These samples were analysed for their ability to induce oxidative damage by two different methodologies, namely **Plasmid Scission Assay (PSA)** and **Dichlorodihydrofluorescin assay (DCFH)**, two complementary and easily adapted techniques for the elucidation of PM-ROS generating capacity. These analyses were carried out during a two-month stay at the University of Cardiff, Wales, UK. The internship was funded by the Spanish Research Council (CSIC) and supervised by Prof. Tim Jones and Prof. Kelly Bérubé.

For the **PSA**, a plasmid ΦX174 RF DNA molecule (phiX174, RF DNA, Promega) susceptible to be damaged by ROS and metals which convert the supercoiled, undamaged isoform to relaxed and linear isoforms (Greenwell et al., 2002; Moreno et al., 2004; Koshy et al., 2007) was selected for use in the PSA (Figure 2.13). Atmospheric particulate samples (1mg) were diluted in molecular grade water and incubated with 200 ng ΦX174 RF DNA in a final volume of 20 µl (n=4). Negative controls were established using incubations of DNA in molecular grade water and positive control consisted of restriction enzyme PstI digest. Samples were gently agitated for 6h before adding 3.33 µl loading dye (blue/orange Loading Dye, 6X, Promega) and electrophoresed on a 0.6% agarose 0.25% ethidium bromide gel (30V, 16h) in 1 x Tris-Borate-EDTA buffer at 30V. Electrophoresed gels were imaged using an UVP Biospectrum Imaging System. This system incorporated a high resolution Hamamatsu 12 bit CCD camera and VisionWorks® software (Ultraviolet Products Ltd., UK); densitometric analyses were performed with Genetools® software (Syngene® Systems, UK).

The relative amount of damaged DNA (relaxed open circle form plus linearised form) in each lane was calculated as a percentage of the supercoiled intact DNA (Koshy et al., 2007). Gels with less than 10% damage in the water controls were accepted for analyses. The data was fitted on a non-linear regression logarithmic model, and the concentration of atmospheric particulate matter to produce 50% damage (TD_{50}) determined (Greenwell et al., 2002).

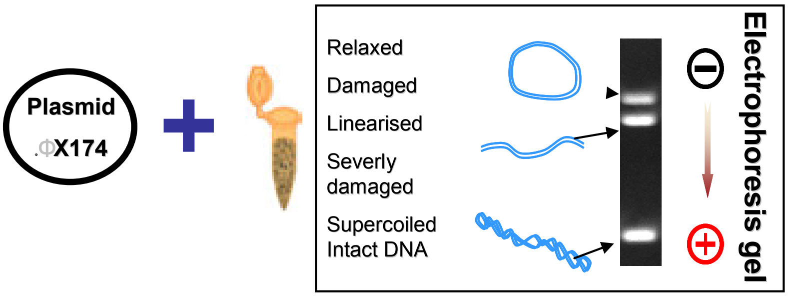

Figure 2.13. Plasmid Scission Assay of ΦX174 RF DNA incubations, incubations with atmospheric particulate matter. The direction of DNA migration from cathode to anode is indicated, with the conformations at varying levels of progressive damage; (Greenwell et al., 2002).

On the other hand, the **DCFH** method exploits the oxidation of DCFH to 2'-7'-dichlorofluorescen (DCF); a strongly fluorescent moiety. The compound was sourced as 2,-7,-dichlorodihydrofluorescein diacetate (DCFH-DA, Sigma-Aldrich, UK), due to the increased stability of the precursor, which was chemically cleaved to the working form of DCFH. This compound has been widely used as a marker of cellular oxidative stress and as an indicator of reactive species formation (Gomes et al., 2005; Koshy et al., 2007). A working solution of DCFH was prepared from DCFH-DA using the method of Cathcart et al. (1983). In brief, 2 ml 0.01M NaOH was added to 8 ml 1 mM DFH-DA in methanol, and this hydrolysate was allowed to react at ambient temperature in the dark for 30min prior to neutralization with 10 ml 25mM NaH_2PO_4 (pH 7.4), providing a 40 µm stock solution of activated DCFH ($\lambda_{excitation}$=498nm; $k_{emission}$=522nm). Reactions were carried out at 37ºC for 25 min in light-resistant eppendorfs, containing 750 µl undiluted particulate matter and a final concentration of 1 mH activated DCFH. For each PM sample, four different dilutions were analysed (500, 200, 100, 50 and 25 µg ml^{-1}).

Fluorescence intensity was measured in a Cary Eclipse Fluorimeter with excitation wavelength at 450 nm and emission wavelengh at 530 nm. Measuring the fluorescence of each pre-incubation confirmed the absence of interfering organic compounds in particulate matter samples. All samples emitted background levels of fluorescence prior to addition of DCFH. Parallel incubations were performed with 1.86 ml 25 mM NaH_2PO_4 (pH 7.4), containing a final concentration of 1µM activated DCFH. This provided a measure of the extent of dye auto-fluorescense. In order to correlate the fluorescense of samples to "equivalents of H_2O_2", an indicator of oxidative stress, a linear calibration curve of H_2O_2 was generated.

- Lung-deposited Surface Area determination (2011-2012).

These measurements aimed to characterize the time variation of the lung-deposited surface area, as toxicity appears to be associated with surface chemistry and the larger specific surface area of ultrafine particles (Oberdörster et al., 2005; Stoeger et al., 2006). This study was carried out at the urban background sampling site previously identified as Palau Reial (41º23'13.08''N 02º06'50.11''E), in close proximity (<100m) to the TG site, and therefore also influenced by the emissions from vehicles in the Diagonal Avenue.

Instrumentation

The lung-deposited surface area (LDSA) concentration is defined as the particle surface area concentration per unit volume of air, weighted by the deposition probability in the lung (Fierz et al., 2011). Particularly discussed are the tracheobranchial and the alveolar region, because of the inefficiency of clearing mechanism and the possible transfer to the blood circulation system with resulting distribution in several end organs. Particle deposition curves are strongly dependent on individual characteristics and physical activity. Therefore, the most usual conditions for LDSA values estimations are:

- Breathing type: nose only
- Functional residual capacity: 3301cc
- Breathing rate: 20 Breath min^{-1}
- Ventilation rate: 1.5 m^3 h^{-1}
- Activity level: light exercise

Measurements of this parameter were taken as the diffusion charger response of atmospheric particles, measured by means of a Nanoparticle Surface Area Monitor (NSAM, model 3550, TSI; Figure 2.14), operating on a 5-minute time resolution and set to simulate the deposition in the alveolar region. This instrument uses a corona discharge to produce positively charged ions and mixes these ions with particles in an opposed flow mixing chamber. An ion trap is located downstream of the mixing chamber. The particles are deposited on a HEPA filter inside a Faraday cup and the current, induced by the deposited particles, is measured with an electrometer.

Between the mixing chamber and particle filter, all excess ions are removed in the ion trap by means of an electric field. Due to the high electric mobility of ions, the voltage can be relatively low. Even though the electric field strength within the ion trap is very low, some charged particles near the electrode of opposite polarity are also removed. Since in the human respiratory tract some particles also get lost before they reach the lung, the ion trap voltage can be adjusted such that the particle losses in the ion trap match those in certain areas of the human inhalation system. It is found that the response function of NSAM matches the surface area deposited in the tracheobronchial region with an ion trap voltage of 100 V, whereas the response function simulates the deposition in the alveolar region with an ion trap voltage of 200 V.


Figure 2.14. NSAM for on-line measurements of LDSA.

The LDSA measurements were complemeted by meteorological data from the Faculty of Physics of the University of Barcelona, and by BC, N and PM_{10}, $PM_{2.5}$ and PM_1 concentrations measured following the technical specifications in the section describing the continuous measurements.

2.3. UNCERTAINTIES AND DETECTION LIMITS FOR AMBIENT AIR CONCENTRATIONS

The above mentioned procedures for the determination of chemical constituents from PM filters are characterized by some degree of uncertainty. The standard deviation among a number of samples shows how much variation or "dispersion" exists from the average (mean, or expected value). However, when individual concentrations are taken, an individual estimate of uncertainty is needed.

The uncertainties contributing to the overall one are that associated with the analytical determination, the air volume sampled, blank variability, filter handling, etc. The uncertainty associated with the analytical procedure is likely to be one of the most important sources and for this reason it was experimentally determined using a similar methodology that the one described by Thompson and Howarth (1976), obtaining a functional relationship between amount of analyte and its corresponding uncertainty (Amato, 2010). The equation chosen for fitting these results was:

$$\sigma_a^2 = \sigma_0^2 + (\alpha \cdot m)^2 \qquad (2)$$

where σ_a is the uncertainty associated with analytical procedure, m is the mass of analyte in the filter while σ_0 and α are fitting parameters. The σ_a values were estimated by repeating several times the complete sample preparation and analysis for 35–60 samples (depending on the number of possible repeats) (Escrig et al., 2009).

The analytical determination includes the subtraction of blank filters which, due to the destructive nature of the analysis, were different filters from the sampled ones for each batch of samples. This causes an additional source of uncertainty σ_{BLK} that has to be propagated jointly with σ_a to obtain the determination uncertainty σ_{A}:

$$\sigma_A^2 = \sigma_a^2 + \sigma_{BLK}^2 \tag{3}$$

With the objective of including additional sources of uncertainty, the overall uncertainty was expanded by the following formula:

$$\sigma_{ij}^2 = \sqrt{\frac{\sigma_A^2}{V_i^2} + (\beta \cdot x_{ij})^2} \tag{4}$$

being V_i the air volume sampled and β a coefficient that was estimated to be 0.15 which might accounts for the error in the flow rate.

The detection limit is the lowest quantity of a substance that can be distinguished from the absence of that substance (a blank value) within a stated confidence limit (generally 1%). In this study, DL was estimate for the j$^{\mathrm{th}}$ analyte basing on the formula performed by Amato (2010):

$$DL_J = \frac{\sqrt{\sigma_{0j}^2 + \sigma_{BLKj}^2}}{V} \tag{5}$$

which consists in propagating the uncertainty linked to the instrument (ICP-MS, ICP-AES, HPLC, etc.) and the blank subtraction (IUPAC, 1995); V is the average value of air volume sampled in 24 hours.

2.4. SOURCE APPORTIONMENT TECHNIQUES

The fundamental principle of source/receptor relationships is that mass conservation can be assumed and a mass balance analysis can be used to identify and apportion sources of airborne PM in the atmosphere. This methodology has generally been referred to as receptor modelling (Hopke, 1985; 1991). The approach to obtaining a data set for receptor modelling is to determine a large number of chemical constituents such as elemental concentrations in a number of samples. A mass balance equation can be written to account for all *m* chemical species in the *n* samples as contributions from *p* independent sources:

$$x_{ij} = \sum_{k=1}^{p} g_{ik} f_{jk} \qquad \text{i=1,2,…..,m} \qquad \text{j=1,2,…...,n} \tag{6}$$

where x_{ij} is the i^{th} elemental concentration measured in the j^{th} sample, f_{jk} is the gravimetric concentration (ng mg^{-1}) of the i^{th} element in material from the k source, and g_{ik} is the airborne mass concentration (mg m^{-3}) of material from the k source.

The question is what information is available to solve equation (6). It is assumed that the ambient concentrations of a series of chemical species have been measured for a set of PM samples so that the x_{ij} values are always known. If the sources that contribute to those samples can be identified and their compositional patterns measured, then only the contributions of the sources to each sample need to be determined. These calculations are generally made using the effective variance least squares approach incorporated into the EPA's CMB (Chemical Mass Balance) model (http://www.epa.gov/scram001/receptor_cmb.htm). However, for many locations, the sources are either unknown or the compositions of the local particulate emissions have not been measured. Thus, it is desirable to estimate the number and compositions of the sources as well as their contributions to the measured PM. The multivariate data analysis methods that are used to solve this problem are generally referred to as factor analysis (FA). The goal of FA is to determine the true dimensionality of the data and the relationships among the measured variables. The pioneers on incorporating this analysis in aerosol mass apportionment used VARIMAX rotated Principal Component Analysis (PCA) in order to determine both sources of particulate mass and also their contributions (Henry and Hidy, 1979; Thurston and Spengler, 1985).

These techniques are based on the Singular Values Decomposition, selecting the eigenvectors to explain the greater part of the variance in the data. With this procedure the factors that minimize the Euclidian length of the residuals of the model (6) are obtained (ordinary Least Squares solution). Although in FA columns of the data matrix are scaled in order to give similar importance to all the variables, this scaling is not optimal because some species can be determined more precisely than others. It is for this reason that Paatero and Tapper (1994) suggested the use of a Weighted Least Squares scheme with the aim of obtaining a minimum variance solution of (6). They demonstrated that the optimum scale of the data matrix is achieved when each individual datum is weighted by the corresponding error estimate. However, this weighted is not solved by eigenanalysis, being necessary to minimize numerically the object function:

$$Q = \sum_{i=1}^{m} \sum_{j=1}^{n} \frac{(x_{ij} - \sum_{k=1}^{p} g_{ik} f_{jk})^2}{\sigma_{ij}^2} \qquad (7)$$

where σ_{ij}^2 is the uncertainty estimate for the especies j measured at time *i*.

Additionally, they proposed to incorporate the basic physical constraint of non negativity of g_{ik} and f_{jk}, calling their approach Positive Matrix Factorization (PMF) (Paatero and Tapper, 1994), which can be performed by the program PMF2 released by Paatero (1997). PMF2 is a model, which implements a weighted least squares approach to perform positive matrix factorisation of measured data. PMF2 solves the 2-way bilinear model, while a second program, PMF3, has also been developed for the solution of 3-way trilinear models. The programs provide a number of options to control the solutions process which are specific to factor analysis.

However, Positive Matrix Factorization can also be solved with the Multilinear Engine (ME-2), which is a more recent technique developed by Paatero (1999) for fitting multilinear and quasi-multilinear mathematical expressions or models to two-, three- and many-dimensional data. The main differences of this program are described in Paatero (1999) and briefly listed below:

-The actions of ME-2 are defined in a “scrip file” written in a special-purpose programming language, allowing incorporating additional tasks such as data processing, etc.

-In ME-2 a priori information can be included as auxiliary terms of the object function to be minimized. Thus, the a priori information is incorporated as a target to be approximately accomplished.

-The Gauss Newton scheme is solved in the ME-2 by the Conjugate Gradient algorithm (Hestenes and Stiefel, 1952), taking advantage of the sparse structure of the Jacobian matrix of the multilinear model.

-The non-negativity of g_{ik} and f_{jk} is achieved in ME-2 by inversely preconditioning of the Conjugate Gradient (Paatero, 1997).

These characteristics of ME-2 make it especially suitable for source apportionment studies were some *a priori* knowledge (chemical ratios, profiles, mass conservation…) of involved sources is available. One of the innovative features of ME-2 (with respect to customary PMF) is that missing data can be easily handled without influencing heavily on the results of the source apportionment. Other programs such as PMF2 or EPA PMF v3.0 do not accept `empty cells`, so only three alternatives are possible: exclude the whole sample, exclude the whole species, replace by median of the species. Therefore ME-2 does not create the equations for the empty cells, permitting to include species that have not been analyzed for the whole period in the analysis.

In ME-2 a priori information must be handled in form of equations, termed as auxiliary equations by Paatero (1999). As indicated, auxiliary equations are included as additional terms Q_{aux} in an enhanced object Q_{enh}

$$Q_{enh} = Q + Q_{aux} \tag{8}$$

One of the simplest forms of auxiliary equation is the "pulling equation" (Paatero and Hopke, 2009), consisting in pulling a f_{jk} (for instante) toward the specific target value a:

$$Q_{aux} = \frac{(f_{jk} - a)^2}{\sigma_{aux}^2} \tag{9}$$

being σ_{aux}^2 the uncertainty connected to the pulling equation, which expresses the confidence of the use of this equation.

2.4.1. Biomass burning emissions detection

In the present study a special-purpose ME-2 script was prepared in order to quantify the contribution of biomass burning to the annual PM mass in Barcelona during 2009. The species were selected based on the uncertainty estimate described in the previous section, which allow separating species which retain a significant signal from the ones dominated by noise. This principle is based on the signal-to-noise S/N ratio described by Paatero and Hopke (2003). However, due to the sensitivity of S/N to sporadic values much higher than the level of noise, the percentage of data above detection limit (ADL) was used as complementary criterion. With the selected set of data, a unique (two-dimensional) input matrix was used, incorporating PM_1, $PM_{2.5}$ and PM_{10} samples. Even though this implies no investigation of the fractionation of pollutants among the three particle sizes, this approach was followed since previous studies showed a significant improvement of results due to the larger number of observations (Amato et al., 2009a). Following this approach requires specific auxiliary equations (Amato et al., 2009a) in order to avoid source contributions higher in $PM_{2.5}$ than in PM_{10}. Thus, an inequality was implemented by the use of an auxiliary object function given by:

$$Q_{aux} = \frac{(g_{ik}(PM_{10}) - g_{ik}(PM_{2.5}))^2}{\sigma_{aux}^2} \text{ if } g_{ik}(PM_{10}) < g_{ik}(PM_{2.5}) \quad (10)$$

$$Q_{aux} = 0 \text{ if } g_{ik}(PM_{10}) \geq g_{ik}(PM_{2.5})$$

Another mass conservation principle is that the sum of analyzed species concentration in one factor does not exceed unity (see Amato et al., 2009a). Such a constraint, even if trivial, is often unaccomplished by standard PMF results (Wu et al., 2007; Amato et al., 2009a). Therefore equations to solve this problem were introduced.

Experimental source profiles were also used as targets to be achieved by the model within a given empirical uncertainty. In particular target profiles were used for the road dust source (Amato et al., 2009b) and sea salt (http://www.epa.gov/ttnchie1/software/speciate). Scaling indeterminacy must be considered when introducing target concentrations. Therefore we fixed the desired metrics of the factor elements by introducing the PM concentration as the first variable in the data matrix and the elements of the first row of factor profile matrix were set to 1, by means of the key values. Finally, based on previous studies (Puxbaum et al., 2007; Caseiro et al., 2009) experimental concentrations and ratios observed for biomass burning sources were introduced: upper limits for ammonium (100 ppm) and for K^+ (8%), lower limit for OC (60%) and target OC/levoglucosan ratio of 6.1±0.3, the average value obtained from the compilation of Puxbaum et al. (2007) of different types of biomass combustion from recent studies. Uncertainties of the source contributions estimates are expected to be higher in summer, spring and fall than in the winter period. This is because levels of levoglucosan were often below the detection limit in summer and were not measured during fall and spring and also because the same target OC/levoglucosan ratio was applied to all seasons (whilst it might be more specific of winter wood burning).

Uncertainties in factor profiles were estimated by bootstrapping (Efron and Tibshirani, 1986). Based on the one available from the EPA PMF3.0 script, (bsmode=15), the bootstrapping consisted in three different steps: re-sampling, reweighting and random rotational pulling. Details can be found in Amato et al. (2009a). The estimation of the uncertainty of the annual mean contribution of the detected sources to PM levels was calculated as the sum of the uncertainty of single species contributions, increased by a factor accounting for the unexplained mass in each factor profile. Results from this analysis are reported in chapter 6.

2.4.2. Human health risk estimates

With the aim of obtaining the cancer risk assessment of the samples collected at IJA during the sampling campaign for the aerosols bioreactivity evaluation (2008-2009), a special purpose ME-2 script was developed in order to build a constrained PMF. The following constraints were introduced: i) Target source profiles for the road dust (Amato et al., 2009a) and the sea salt (SPECIATE) factors; ii) a mass conservation principle consisting in: higher the PM size fraction, higher the source contribution; iii) sum of species concentrations in a source profile must be less than 1; iv) a fixed value (1.7) for the S/NH_4^+ ratio and a maximum content of 10% of OC in the secondary sulphate factor.

In this study we also calculated the mean contribution (c_{jk}) of each source (*Kth*) to the measured concentrations of individual pollutants (*jth*) with the following equation:

$$c_{jk} = f_{jk} \times \breve{g}_k \qquad (11)$$

where f_{jk} is the concentration of the *jth* species in the *Kth* source profile, and $\breve{g}_k$ is the mean contribution to PM from the *Kth* sources.

With c_{jk}, the cancer risk from exposure to the *Kth* source (*Rk*) can be calculated as the sum of risks of all available species in its source of feature following the methodology of Wu et al. (2009):

$$R_K = \sum (c_{jk} \times UnitRisk_j) \qquad (12)$$

In this work, only those metals and PAHs which have known toxicity values were considered. We assumed that the only route of exposure is through inhalation. Their toxicities are then reported in terms of their inhalation unit risk (UR), (µg m^{-3})$^{-1}$. UR is defined as the upper-bound excess lifetime cancer risk estimated to result from continuous exposure to an agent at a concentration of 1 µg m^{-3} in air (EPA, 2011). UR values for each species were taken from the Integrated Risk Information System, the California Environmental Protection Agency and the USEPA Regional Screening Level. Results from this analysis are reported in chapter 7.

2.5. INTERPRETATION OF THE ORIGIN OF AIR MASSES

In order to accurately interpret the variability of PM levels, a detailed analysis of the different meteorological scenarios during the sampling period was required. To this end, different tools and meteorological and aerosol maps were used. All of them are available online for free.

- Back-trajectory analysis: Hysplit model

Air mass back-trajectories analysis was performed at 750, 1500 and 2500 m.a.s.l. using the Hysplit model (Hybrid single Particle Lagrangian Integrated Trajectory Model; Draxler and Rolph, 2003; http://www.arl.noaa.gov/HYSPLIT.PHP). The HYSPLIT model is a complete system for computing simple air parcel trajectories to complex dispersion and deposition simulations. From the back-trajectories (calculated for 120 hours) it is possible to establish the origin of air masses that reach a determined area when these are transported from a long distance. For the study area, the distinguished origins were: Northern Atlantic, North-western Atlantic, Western Atlantic, South-western Atlantic, Mediterranean, Centre Europe and Regional or Winter Anticyclonic episodes. Back-trajectory analysis was carried out on a daily basis for the period 2008-2011.

-Boundary layer depth

Boundary layer depths were calculated for the different areas using the meteorological model of NOAA Air Resources Laboratory (ARL, www.arl.noaa.gov/readyamet.html) by introducing the geographical coordinates of the site. In the menu Stability time series, a meteorological data file (GDAS or FNL) must be selected. Then, the starting date and time must be introduced and the duration of the stability plot chosen. The boundary layer depth was carried out on a basis of three hours for the period 2008-2011.

- Aerosol concentration maps

The **NAAPS** model produces aerosol maps from the Marine Meteorology Division of the Naval Research Laboratory (NRL, http://www.nrlmry.navy.mil/aerosol). These provide information on the aerosol optical depth and the surface concentration of mineral dust from desert areas, sulphate particles and carbonaceous aerosols derived from biomass burning. There are four daily maps (0, 6, 12 and 18h) with prediction up to 96 hours.

SKIRON simulations produce also aerosol surface concentrations maps (http://forecast.uoa.gr/dustindx.php, Kallos et al., 1997), providing information on total column loads and surface level dust and in addition dry and wet dust deposition fluxes at a surface level.

BSC-DREAM model (http://www.bsc.es/projects/earthscience/DREAM/, Nickovic et al., 2001) produces also surface and column dust concentration maps, as well as dry and wet deposition fluxes. The forecasting maps are made of a meteorological map with surface pressure and rainfall, and an aerosol map showing areas affected by dust and expected concentrations at a surface level.

CHAPTER 3: Peculiarities in atmospheric particle number and size-resolved speciation in an urban area in the western Mediterranean

Chapter 3. Peculiarities in atmospheric particle number and size-resolved speciation

Parts of the results presented within this chapter have been published in Atmospheric Environment, 2011; 45: 5282-5293: Peculiarities in atmospheric particle number and size-resolved speciation in an urban area in the western Mediterranean: Results from the DAURE campaign.

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3. PECULIARITIES IN ATMOSPHERIC PARTICLE NUMBER AND SIZE-RESOLVED SPECIATION IN AN URBAN AREA IN THE WESTERN MEDITERRANEAN

ABSTRACT

Air quality degradation problems in urban environments are mainly due to road traffic emissions. In northern and central European cities extensive investigations have been carried out on the variability of number of ultrafine particles and Black Carbon, whereas studies in southern-Europe have traditionally focused on chemical speciation, resulting in insufficient information to characterise urban aerosol processes. Accordingly, sources and processes controlling atmospheric pollutants were evaluated during the international DAURE campaign by means of continuous measurements of particle number, Black Carbon, PM_x, particulate nitrate and particulate sulphate concentrations. Results provided evidence of the influence of three PM sources of interest: road traffic, construction-demolition works and shipping emissions. Road traffic governs the daily cycle of Black Carbon, a number of gaseous pollutants and the finer fraction of PM. Evaluation of the coarse aerosol ($PM_{2.5-10}$) daily cycle furnished evidence of the influence of construction-demolition works. These activities could increase hourly $PM_{2.5-10}$ levels by up to 8 µg m^{-3} on an annual mean basis based on hourly aver. Finally, shipping emissions were traced by means of SO_2 concentrations, which peak at a time different from that of other gaseous pollutants owing to the regular daytime onshore breeze bringing harbour emissions at midday. Moreover, a major local contribution of secondary aerosols was detected with elevated particle number levels at midday when nucleation processes are favoured by photochemistry and lower pollution levels. Particle number data were also analysed in search for the primary emission of vehicle exhaust (N1) and the secondary parts from gaseous precursors, primary parts from non-traffic sources, and/or particles inherited in the air mass (N2). N2 fraction accounted for 40% of number concentrations, ranging from 37% during the morning rush hour to 61% at midday. Results proved that the combination of PM_{10} and BC monitoring in urban areas may constitute a good approach to evaluate the traffic impact on air quality (BC), considering also the influence of other primary and secondary sources (PM_{10}).

Keywords: City-works, Demolition, Urban, Nucleation, Coagulation, Shipping emissions.

3.1. INTRODUCTION

Vehicular traffic has been shown to be the major source of primary atmospheric particulate matter (PM) and certain gaseous secondary PM precursors (NOx, CO, VOCs) in most urban European environments (Harrison and Yin, 2008; Querol et al., 2008; Viana et al., 2008). Road traffic is also a major source of organic secondary PM (Dunlea et al., 2009; Jiménez et al., 2009; Renner et al., 2010). Diesel vehicles are an especially significant source of fine and ultrafine particles, exceeding the emissions from gasoline vehicles by a factor of >10 in terms of mass concentration and > 10^5 times in terms of number concentration (Harris and Maricq, 2001). This difference has been reduced a lot by EURO 5 and EURO 6 vehicles, but diesel cars still may emit higher number of particles than gasoline cars (Ban-Weiss et al., 2009). Approximately 95% of the mass of these particles consists of particles with a diameter <2.5 microns that may be inhaled and become trapped within the small airways and alveolar regions of the lung (ARB, 2008). In certain European countries such as Spain, the use of diesel vehicles has led to a decrease in CO and CO_2 emissions and to an increase in the levels of suspended submicronic PM and NO_2 (Pérez et al., 2010).

European policies on vehicular emissions have focused on reducing primary emissions (exhaust emissions). However, these policies have not proved to be successful in achieving a reduction of PM levels at urban sites (Harrison et al., 2008). In this regard, two factors should be noted: a) the part played by non-exhaust emissions in contributing to increase PM levels. These emissions generate particles, mainly in the coarse fraction ($PM_{2.5-10}$), of which resuspension constitutes a significant source; and/or b) the underestimation of secondary aerosols derived from traffic and other sources. Field studies have provided evidence that secondary aerosols are more abundant than predicted by the models (Volkamer et al., 2006).

A number of studies in northern and central European cities have investigated the aerosol processes governing the variability of ambient concentrations of particle number and Black Carbon (Aalto et al., 1995; Olivares et al., 2007; Yttri et al., 2009). However, in cities in the south of Europe, studies have focused on the assessment of size-resolved (PM_{10}, $PM_{2.5}$ and/or PM_1) chemical speciation data (Querol et al., 2001; Vecchi et al., 2004; Pérez et al., 2008; Querol et al., 2008). Moreover, in the Mediterranean region few studies are available for particle number and Black Carbon (Rodriguez et al., 2008; Rodriguez and Cuevas, 2007; Pey et al., 2008; Pey et al., 2009; Fernández-Camacho et al., 2010; Pérez et al., 2010). A combination of the above air quality monitoring parameters may provide detailed information on the atmospheric processes controlling the variability of the urban Mediterranean aerosol, which depends on different emission sources and processes. One of these sources is construction and demolition works, which is especially relevant in dry regions. Construction and demolition activities exert an influence mostly at local-scale and on coarse particle concentrations (Deacon et al., 1997; Harrison et al., 2001). To reduce these emissions, it is a common practice to keep surfaces wet, but the fine material may be available for subsequent release (Winiwarter et al., 2009). In Europe, building sites and road works account for a contribution of 2-8% to the annual PM_{10} average (Deacon et al., 1997). In southern-Europe, this contribution may reach higher proportions (up to 20%, as registered in Barcelona by Amato et al., 2009a).

Finally, in coastal urban areas, emissions from commercial shipping (passenger and cargo) may also constitute a relevant source of PM. Diesel engines on ocean going vessels are significant contributors to air pollution in many cities and ports (Lack et al., 2009, Pandolfi et al., 2010). Combustion of fuel oil in ports is an important source of SO_2 emissions with global, regional and local impacts (Derwent et al., 2005). According to global estimates, shipping emits between 0.9 and 1.7 million tons of total suspended particles (TSP) annually affecting coastal areas (Moldanová et al., 2009). Emissions from ship fuel-oil engines mainly consist of organic carbon, ash, sulphate and inorganic constituents from combustion (V, Ni, Ca, Fe) (Moldanová et al., 2009). These emissions may account for 2-4% of the mean annual ambient air PM_{10} levels (25% primary particles and 75% secondary particles) and for 14% of the mean annual $PM_{2.5}$ in Mediterranean urban areas (Viana et al., 2009).

The aim of this work is to assess the impact of these PM emission sources (vehicular traffic, construction/demolition works, and shipping) and aerosol processes on the variability of particle number concentration, Black Carbon (BC) and coarse and fine PM levels, as well as speciation, at an urban site in the western Mediterranean basin. Major atmospheric processes and emission sources affecting the hourly evolution of PM will be identified, with especial emphasis on the formation of secondary inorganic compounds. Furthermore, the simultaneous measurements of N, BC and PM_x allow evaluating their suitability for monitoring the impact of sources with emissions in different size ranges, e.g. traffic (fine and ultrafine particles from exhaust emissions and coarse particles from resuspension), and also of atmospheric processes such as nucleation or coagulation/ condensation.

To this end, continuous measurements were carried out at TG site during February-March 2009. An overview of the campaign, participant and collaborating groups is presented in Pandolfi et al. (2012a). Earlier studies on PM variability and composition in Barcelona may be found elsewhere (Viana et al., 2005 and 2006a; Pérez et al., 2008; Pey et al., 2008). Data from the following instrumentations described in the methodology section will be discussed here: MAAP, WCPC, HR-ToF-AMS, PM optical counters, DIGITEL and MCV high-volume samplers, SMPS, RDI and real-time monitors for gaseous pollutants. In addition, meteorological variables (atmospheric pressure, wind components, solar radiation, temperature and relative humidity) were obtained from a mobile meteorological station. Traffic data were supplied by the Council of Barcelona (Servei de Mobilitat) and Dirección General de Tráfico (DGT).

3.2. RESULTS AND DISCUSSION

3.2.1. Notes on concentrations and variability

Before focusing on the results from the DAURE campaign, it is worth describing the previously reported levels and variability of urban air pollutants in the city, which are briefly explained in chapter 1. This description helps to illustrate which new information can be obtained by the extense instrumentation and the higher temporal resolution of chemical speciation during the DAURE measurements, which allowed extensively understanding the factors influencing the air quality of Barcelona.

With regard to N, the size distribution was studied between November 2003 and December 2004 (Pey, 2007). Results showed two maximum of N concentrations at 7-9h UTC and at 20-22h UTC, coinciding with the traffic rush-hours. In addition, the average diameter for which the size distribution of submicron particles is maximum (DpNmax) decreased notably at 14-15h UTC and it was related to the enhancement of nucleation processes at this time. In 2007, four months of simultaneous measurements of N and BC were collected, a clear increase in N/BC ratio was observed during the central hours of the day and it was again related with photochemical nucleation processes that increased the N levels while the BC levels were reduced by wind speed and direction changes (Pérez et al., 2010). The ratio N/BC was significant higher at weekend, explaining the favoured photochemical nucleation processes that were observed when atmospheric pollutant levels were lower. The contribution of photochemistry enhancing the secondary formation of aerosols has been also the justification for the higher levels of SO_4^{2-} obtained during summer compared to winter in Barcelona (Pey, 2007; Pérez, 2010). At this point of knowledge it was necessary to (1) simultaneously study the N size distribution, the total N concentration and the BC concentrations, (2) to deeply analyse the formation of secondary particles, trying to describe which parameters and compounds are directly governing the nucleation processes in the urban environment of Barcelona.

Figure 3.1 shows the annual daily cycle of $PM_{2.5-10}$, $PM_{1-2.5}$ and PM_1 concentrations from 2003 until 2008. The same daily patterns are observed for every year, with levels mainly influenced by traffic and meteorology (breeze circulations). A detailed description of the patterns is found in Pérez (2010). $PM_{2.5-10}$ levels do not decrease during the day with the ratio traffic/wind speed reaching the minimum at around midday. This increase at midday is important to be analysed from year to year in order to find differences which allow concluding possible associations with meteorology factors and pollution sources.

The daily cycle of NO_X and CO (Figure 3.2) is very similar from year to year, peaking at traffic rush-hours (6-8 h UTC in the morning and 19-20h UTC in the evening). On the other hand, SO_2 levels show a daily cycle with a pronounced maximum at 10-11h UTC (Figure 3.2) which highlights the main impact of a pollution source other than traffic, which is governing the levels and which is important to be studied in detail.

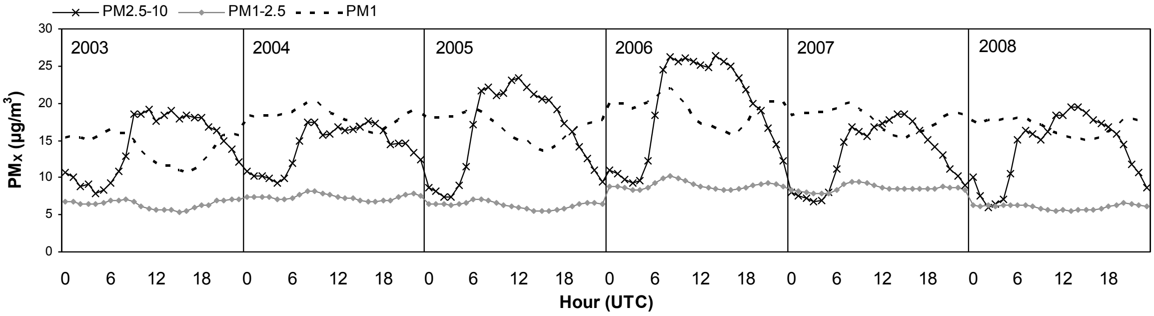

Figure 3.1. Annual daily cycle of $PM_{2.5-10}$, $PM_{1-2.5}$ and PM_1 from November 2003 to December 2008.

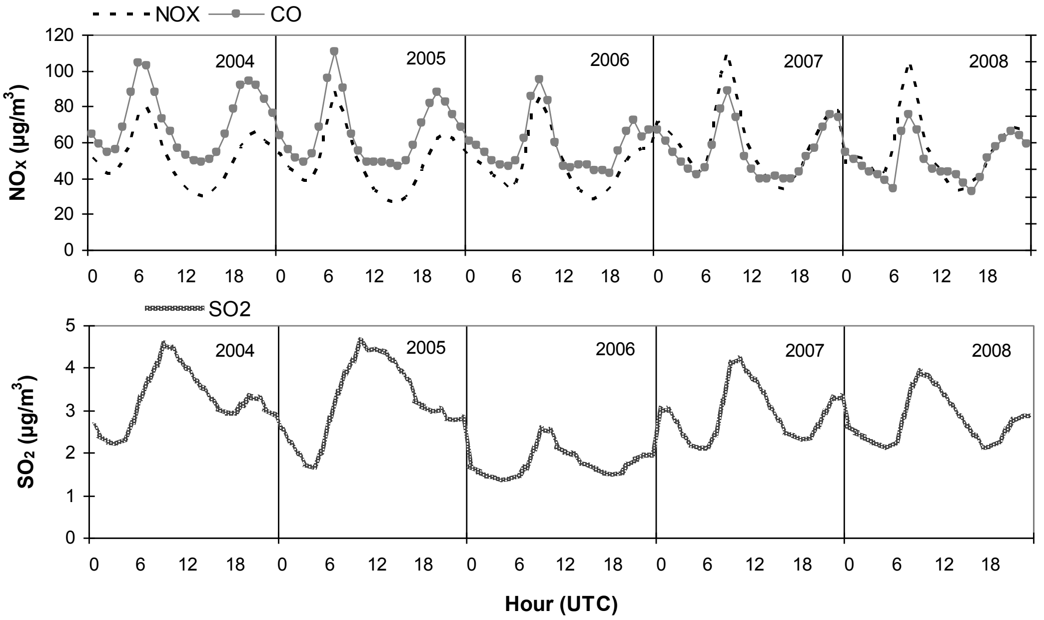

Figure 3.2. Daily cycle of NO_x, CO and SO_2 from January 2004 to December 2008.

On the other hand, it was also necessary to compare the levels of atmospheric components and parameters measured during DAURE with previous measurements performed over the years with the aim of checking if the atmospheric conditions were representative of the typical winter conditions in the area of study. Figure 3.3 shows the mean values of corrected GRIMM PM_1, $PM_{1-2.5}$, $PM_{2.5-10}$ mass concentration levels, NO, NO_2, O_3, and SO_2 levels, temperature (T), relative humidity (RH), solar radiation (SR) and precipitation (prec) calculated during the DAURE compared with the averages calculated over the DAURE (March) sampling period for each year. Averages over 2003-2008 are represented by the horizontal lines in each plot and error bars corresponding to the standard deviation are shown above the 2009 data. Results confirm that the conditions during the campaign were representative of the typical winter conditions, with the majority of the averages within the range of the standard deviation of the 2003-2008 means. The exception was the lack of precipitation during the whole campaign.

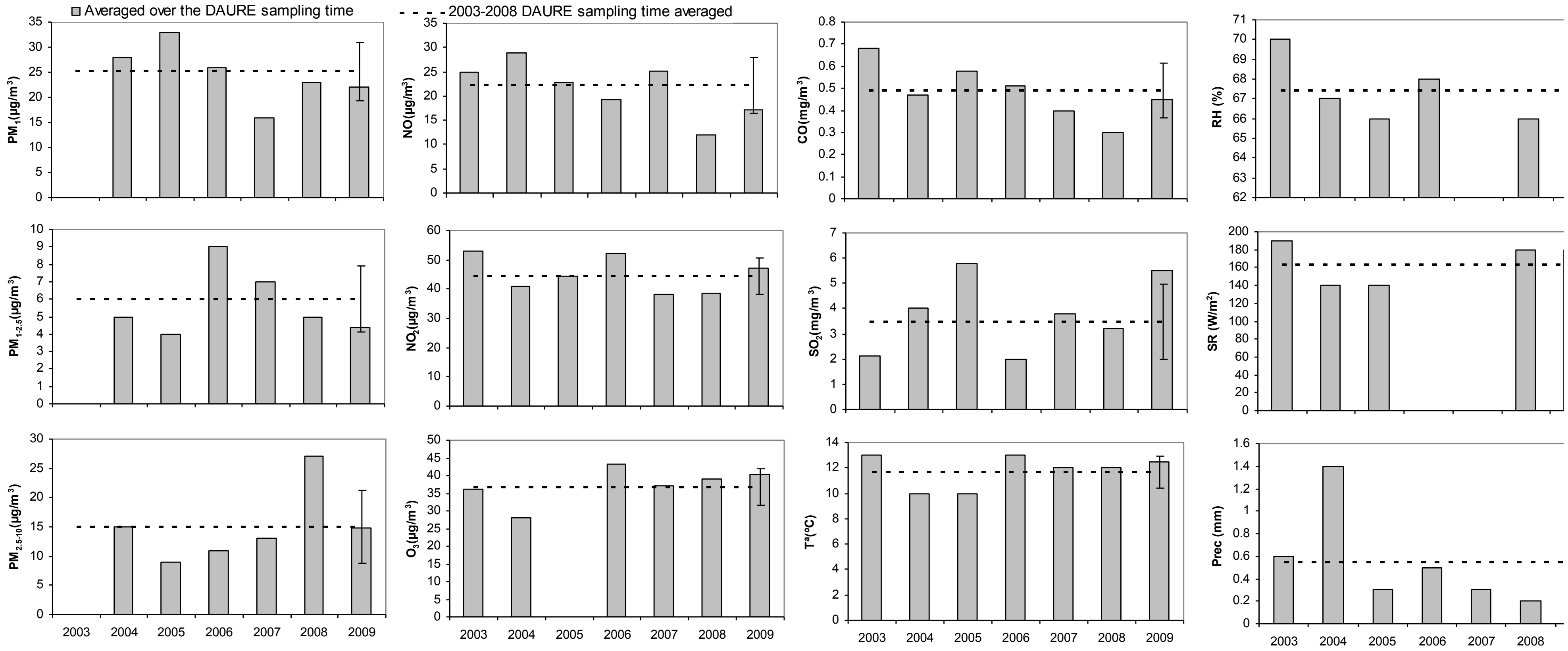

Figure 3.3. Representativity of parameters measured during the DAURE campaign (adapted from Pandolfi et al., 2012a).

3.2.2. Variability of atmospheric pollutant concentrations

A detailed description of the time series of PM levels during the DAURE campaign may be found in Pandolfi et al. (2012a). Three main different meteorological and pollutant transport scenarios (A, B and C) were identified: the B scenarios were defined as periods with persistent anticyclonic conditions with air masses lying over the West Mediterranean Basin (WMB) for days with marked atmospheric inversions causing important accumulation of aerosol at urban levels; during the A scenarios less stagnant conditions and higher boundary layer heights led to slightly lower PM levels compared to the B episodes. Finally, the C scenarios were governed by Atlantic advections episodes, with a prevailing wind direction of 220-260º, which caused the renewal of air masses and decrease pollutant concentrations. These scenarios are frequently reported in the WMB in winter when the location of the Azores anticyclone (placed to the West) favours the entry of Atlantic air masses, thus replacing air masses and reducing levels of atmospheric pollutants. However, during specific winter anticyclonic conditions highly polluted air masses from the coast and valleys are accumulated due to thermal inversions during a few days. The distinction between A and B scenarios is evident from the study of the atmospheric pollutant behaviour in a closed rural background site (Montseny; 41º56'N 02º21'E, 720 m.a.s.l.), since levels increase considerably during A-scenario showing a clear diurnal cycle driven by the sea breeze transporting pollutants toward the rural station in the afternoon favouring at the same time the formation of aerosols during the transport. Thus, for the purpose of the present work, the scenarios were divided into AB and C in the urban area assuming that the scenario AB is governed by the accumulation of aerosols due to medium/strong atmospheric stagnation conditions. Table 3.1 shows the average values and standard deviation of GRIMM corrected PM_x (PM_1, $PM_{1-2.5}$, $PM_{2.5-10}$) mass concentration, Black Carbon levels (BC) and number concentrations (N) during the DAURE campaign, distinguishing both kind of the above described episodes. The relationship between measurements from particles of different sizes allows characterising the influence of different sources in the air quality of the city.

Table 3.1. Average values and standard deviation of GRIMM corrected PM_x (PM_1, $PM_{1-2.5}$, $PM_{2.5-10}$) mass concentration, Black Carbon levels (BC) and number concentrations (N) during the DAURE campaign for the different episodes.

	AB episodes		C episodes	
	Average	**St. Deviation**	**Average**	**St. Deviation**
PM_1(μg/m^3)	25.5 (±1.5^a)	3.2	6.8 (±1.5^a)	1.1
$PM_{1-2.5}$ (μg/m^3)	4.4 (±1.5^a)	0.5	3.9 (±1.5^a)	0.3
$PM_{2.5-10}$(μg/m^3)	15.1 (±1.5^a)	10.3	8.8 (±1.5^a)	4.7
BC (μg/m^3)	2.7 (±12%^{b})	0.9	0.9 (±12%^{b})	0.3
N_{5-1000} (n/cm^3)	21700 (±10%^{c})	4300	16600 (±10%^{c})	4400

[a] Viana et al., (2006b)

[b] Schladitz et al. (2009)

[c] Hering et al., (2005)

Figure 3.4a shows N and BC levels, as well as the ratio N/BC for the entire campaign as a function of the two scenarios. 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., 2001), especially diesel vehicles, which emit particles with a grain size lower than 200 nm (Shi et al., 1999). Thus, the combination of N and BC, as reported in literature may properly evaluate the exposure to road traffic emissions (Harrison and Yin, 2008; Smargiassi et al., 2005; Rodriguez and Cuevas, 2007), as well as the contribution to ultrafine particles levels of sources other than exhaust emissions and of physicochemical processes. A marked decrease in BC is registered during C episodes, with mean daily concentrations of 0.8 µg m^{-3} compared with a mean value of 2.8 µgm^{-3} obtained during AB episodes. This decrease is less pronounced for N, for which average values are 16600 particles cm^{-3} during C episodes and 21700 particles cm^{-3} during AB episodes. These results show a decrease of 71% for BC levels and 30% for N when comparing AB and C days. The lower decrease registered for particle number concentrations suggests a prevalence of aerosol formation by nucleation processes over the levels of primary particles during C episodes. In a cleaner atmosphere, nucleation processes are more likely to occur than coagulation or condensation, especially at midday when photochemistry induces nucleation owing to the higher solar radiation intensity in a thicker mixing layer (Rodríguez et al., 2007b; Pey et al., 2008 and Pérez el al., 2010). These processes are also evidenced by the N/BC ratio (Figure 3.4a), which reaches a maximum during C episodes, attaining values of up to 70000 particles per 1µg m^{-3} BC. The results corroborate the prevalence of secondary aerosol formation in the urban background, with a very important contribution in terms of number. This will be discussed below in greater detail. Levels of NOx and CO (Figure 3.4b) follow the same temporal trend as described for N and BC, with high values during atmospheric stagnation periods (AB) and low levels during Atlantic advection episodes (C). NOx and CO variability is determined by atmospheric dynamics but also by traffic emissions, with a maximum during the morning rush hour. The reduction of road traffic flow intensity during the weekends results in lower morning and evening peaks and in a different evolution of CO and NOx levels. O_3 levels are higher on clean days owing to a lower interaction with other species (NOx, carbonaceous aerosols). Concentrations of SO_2 peak at a time different from that of the other gaseous pollutants, suggesting the influence of a different emission source.

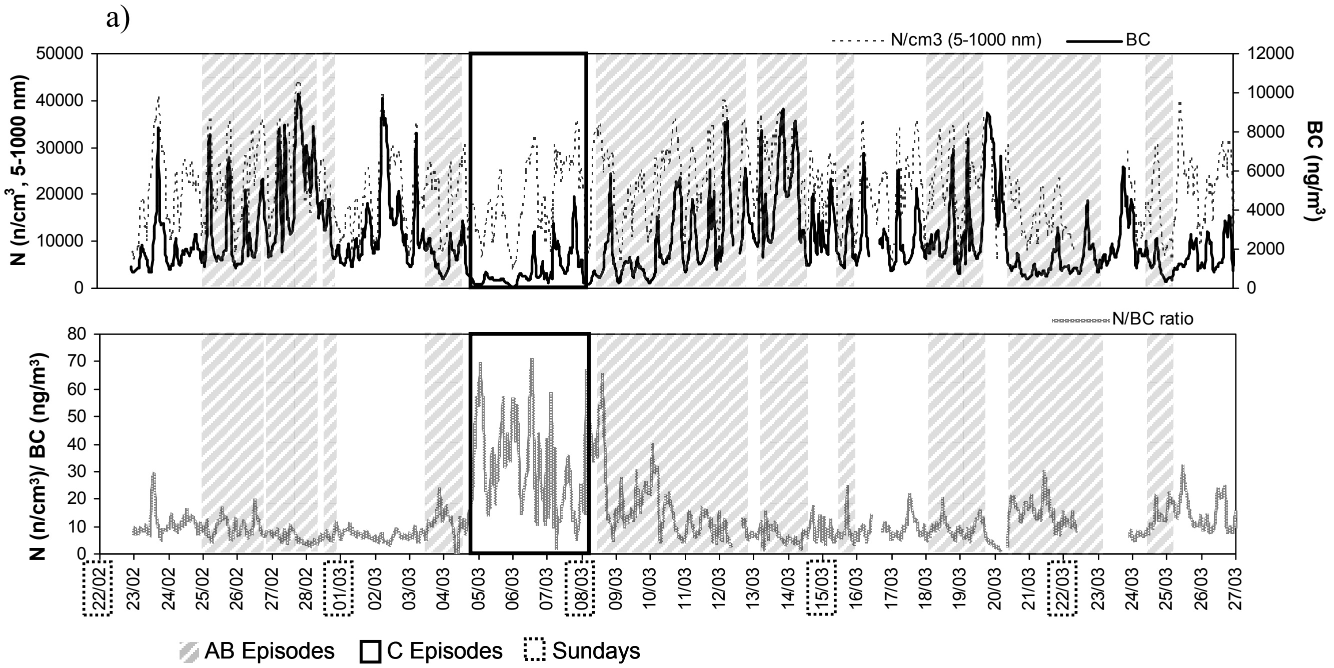

Figure 3.4. Time-series of atmospheric pollutants during the DAURE campaign indicating main pollutant episodes (Pandolfi et al., 2012a). a) Black Carbon (BC), Number concentration (N) and N/BC ratio; b) SO_2, NO, CO and O_3 concentrations.

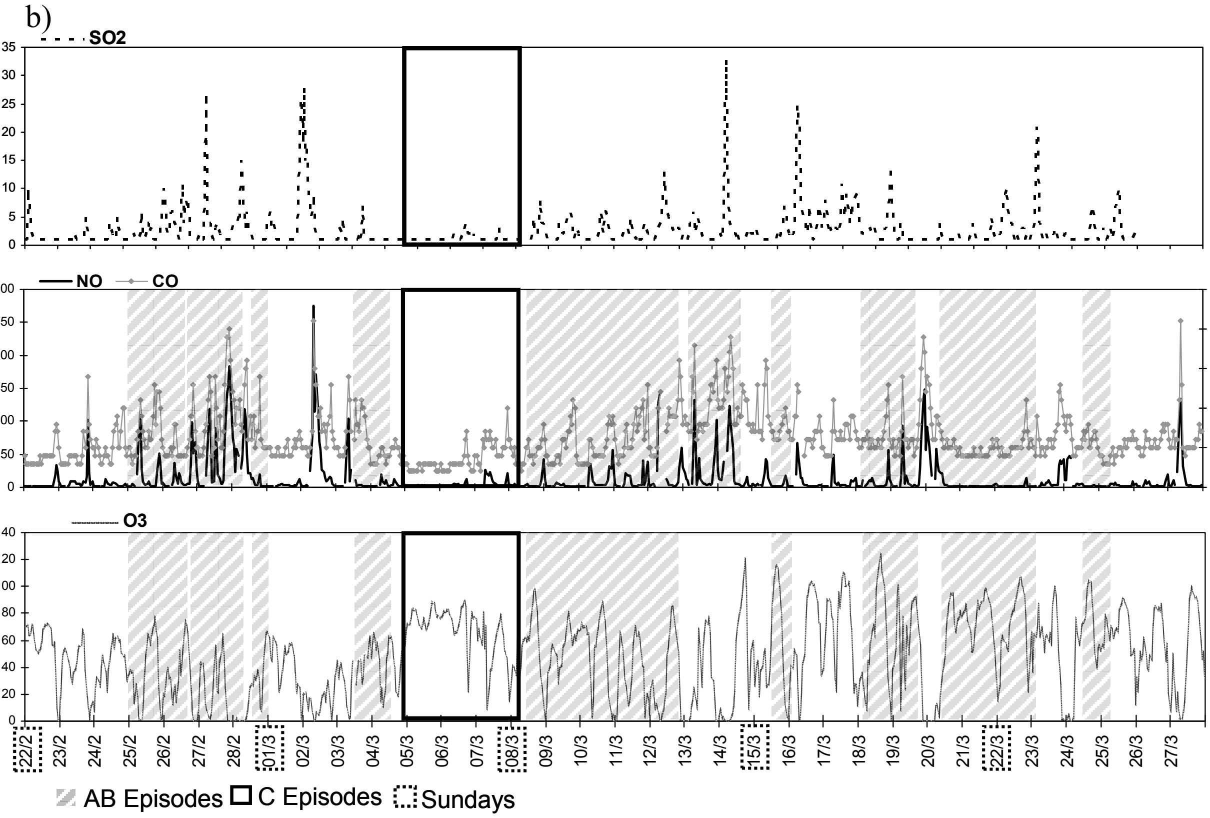

Figure 3.4. Continuation.

3.2.3. Daily cycle of atmospheric pollutants: influence of emission sources

The daily evolution of N and BC at the site under study is highly influenced by traffic emissions (Figure 3.5a), similarities between the cycle of this two parameters, accounting for very different particle sizes, reflect the influence of a common source (vehicle exhaust emissions) (Fruin et al., 2004; Rodriguez and Cuevas, 2007) while differences highlight the impact of local sources other than traffic. Number concentration increases with road traffic intensity in the morning (6-9 h UTC) owing to the primary particles emitted directly by vehicles and formed during dilution and cooling of the exhaust emissions (Maricq, 2007). During AB scenarios, N shows a second peak at midday when high solar radiation and the growth of the mixing layer allow for the dilution of aerosols, resulting in photochemical nucleation processes from gaseous precursors, this phenomenon was also evident by averaging the entire period of the campaign. The nucleation particle size of this midday N peak was evidenced by Pey et al. (2008) and Pérez et al. (2010). Processes of very fine secondary aerosol formation are especially important during Atlantic advection episodes since the cleaner air masses allow coagulation and condensation processes to be reduced, leading to nucleation mediated by photochemistry. However, the strong north-western advection hinders the development of the described daily cycle for N, as during these days this cycle was mainly governed by solar radiation, and maximum were observed at a time different than during the rest of the days (concentrations are around 20000 n cm^{-3} from 11 to 18 h UTC), since wind intensity prevented the development of sea breezes and minimize the impact of vehicle emissions at traffic rush hours. The levels of number concentration at midday during C episodes are about 18% higher than the daily average, while they are between 7% higher and 3% lower than average during AB episodes. In addition, there is a marked difference when comparing days with high and low O_3 concentrations: the number of particles at midday for days with O_3 levels above 60 µg m^{-3} is 22% higher than the daily average, while the number of particles at midday with O_3 levels below 40 µg m^{-3} is <5% higher than the daily average. Traffic peaks are observed in the evening, and at night N falls owing to the decrease in the traffic flow.

The levels of BC follow the same evolution as N levels in the morning, but decrease notably during the middle hours of the day, confirming that the second peak of N could not be a consequence of primary emissions from road traffic, but of secondary formation of particles from gaseous precursors. This sharp BC fall could be attributed to the growth of the mixing layer, reduction in the traffic flow, increase in wind speed associated to the entrance of the sea breeze, and to a change of wind direction during the day from NW to S, related with the development of breeze (Pérez et al., 2010). In the evening, BC levels increase showing a second maximum at 18-21 h UTC, and then decrease during the night owing to the reduction of fresh emissions from vehicles. Thus, hourly variation of BC is much more simultaneous to the traffic flow, whereas N at midday seems to be independent of this source.

The occurrence of the above midday N peak, coinciding with minimum BC levels, suggests a prevalence of secondary aerosol formation due to photochemical nucleation. This is supported by results from an SMPS operating on a 5-min time resolution during the campaign, which showed nucleation events at noon for about 25% of the days. As shown in Figure 3.6, an event occurred on 25th March coinciding with the maximum in solar radiation and it was characterized by a small particle growth between 12-15h and 15-18h local time. It is important to highlight that the SMPS was measuring from 13 nm, so total particle number concentration measured by the CPC (>5 nm) was necessary to confirm that the particle formation took place inside the city. Figure 3.7 shows the polar plots of number size distribution for eight different size ranges and for BC during the whole campaign. The same wind dependency was observed for the particles above

50nm and BC, but smaller particles, especially those in the nucleation mode (<20nm) were detected in higher concentrations for wind velocities above 2.5m/s, which mostly occurred at noon during the campaign (Figure 3.8).

Levels of atmospheric gaseous pollutants from vehicle exhaust emissions (CO, NOx) follow the evolution of traffic intensity, reaching a maximum during the morning rush hour, decreasing during the day because of dilution processes and photochemical reactions, and increasing again in the evening (Figure 3.5b). Levels of CO remain relatively high at night owing to the reduction of the boundary layer height and lower wind speeds that prevent the dispersion of pollutants. During C scenarios, this trend is less marked than in AB episodes because of intense wind conditions. As expected, the evolution of O_3 levels shows an increase at midday, which coincides with that of solar radiation since its formation depends on photochemistry. Maximum levels of this gaseous pollutant are reached on C days owing to the lower ambient NO levels.

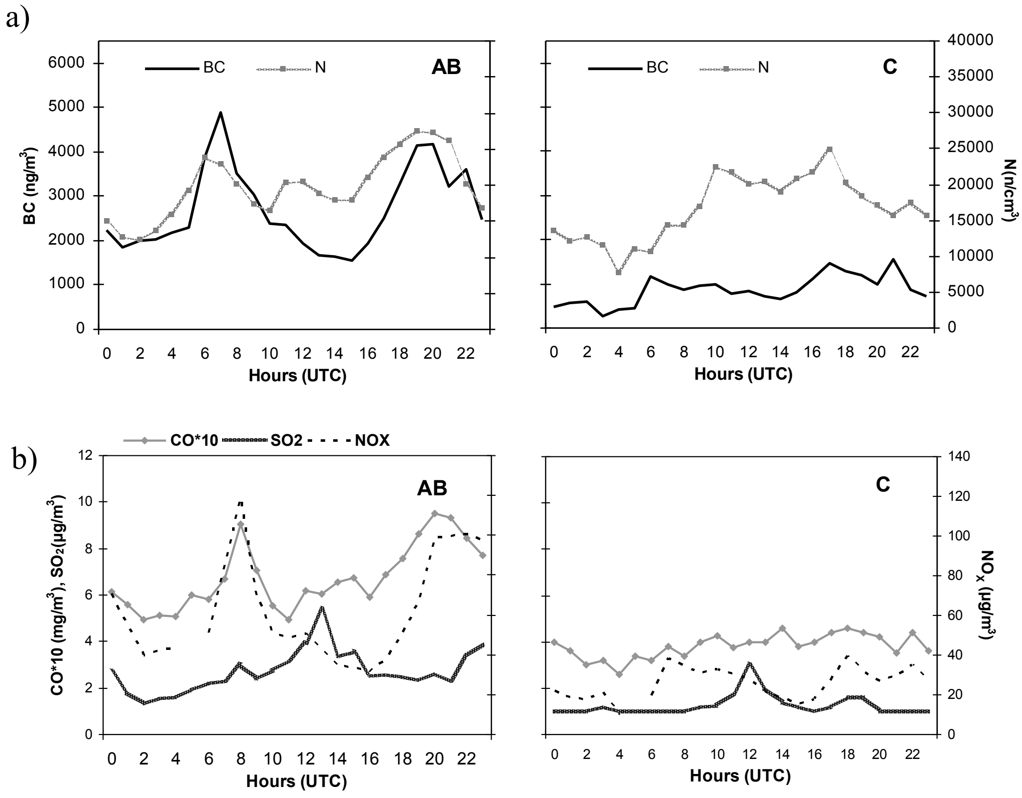

Figure 3.5. Averaged daily cycles of a) Black Carbon (BC) and Number concentration (N) and b) NOx, CO and SO_2 for the whole campaign distinguishing the AB and C scenarios.

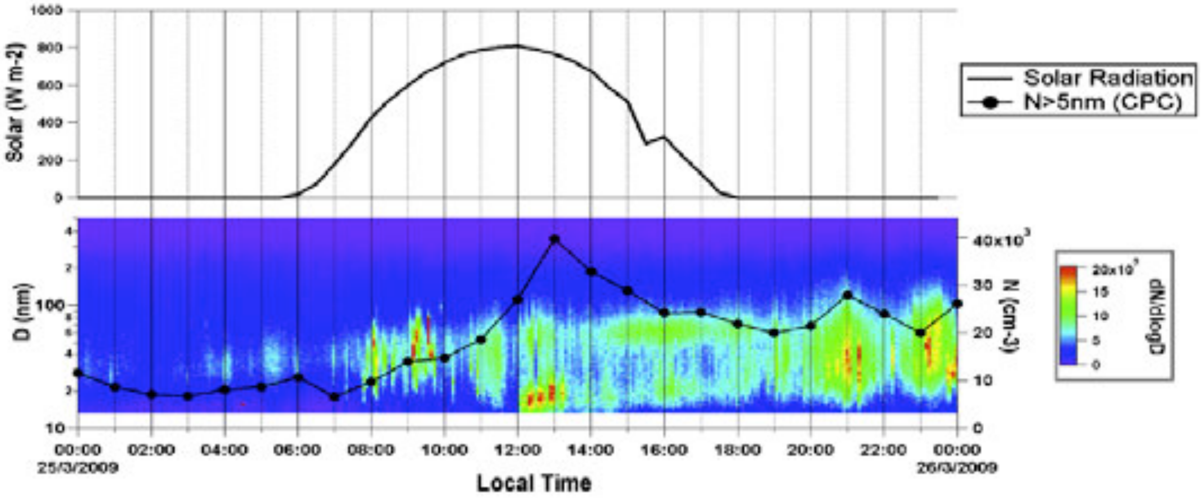

Figure 3.6. Daily variability of the particle number size distribution showing an example of a photochemical nucleation event on 25th March 2009.

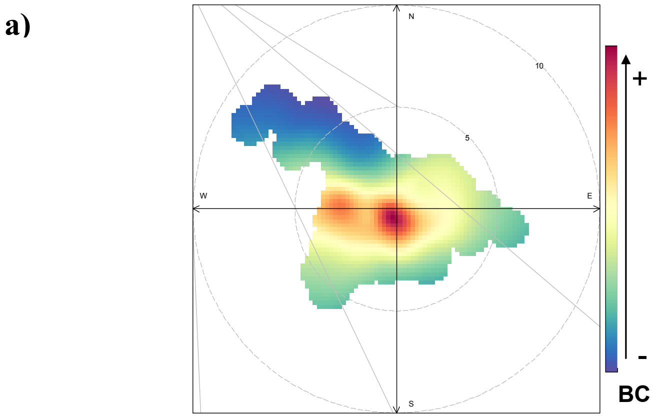

Figure 3.7. Polar plots of: a) BC, b) Number size distribution.

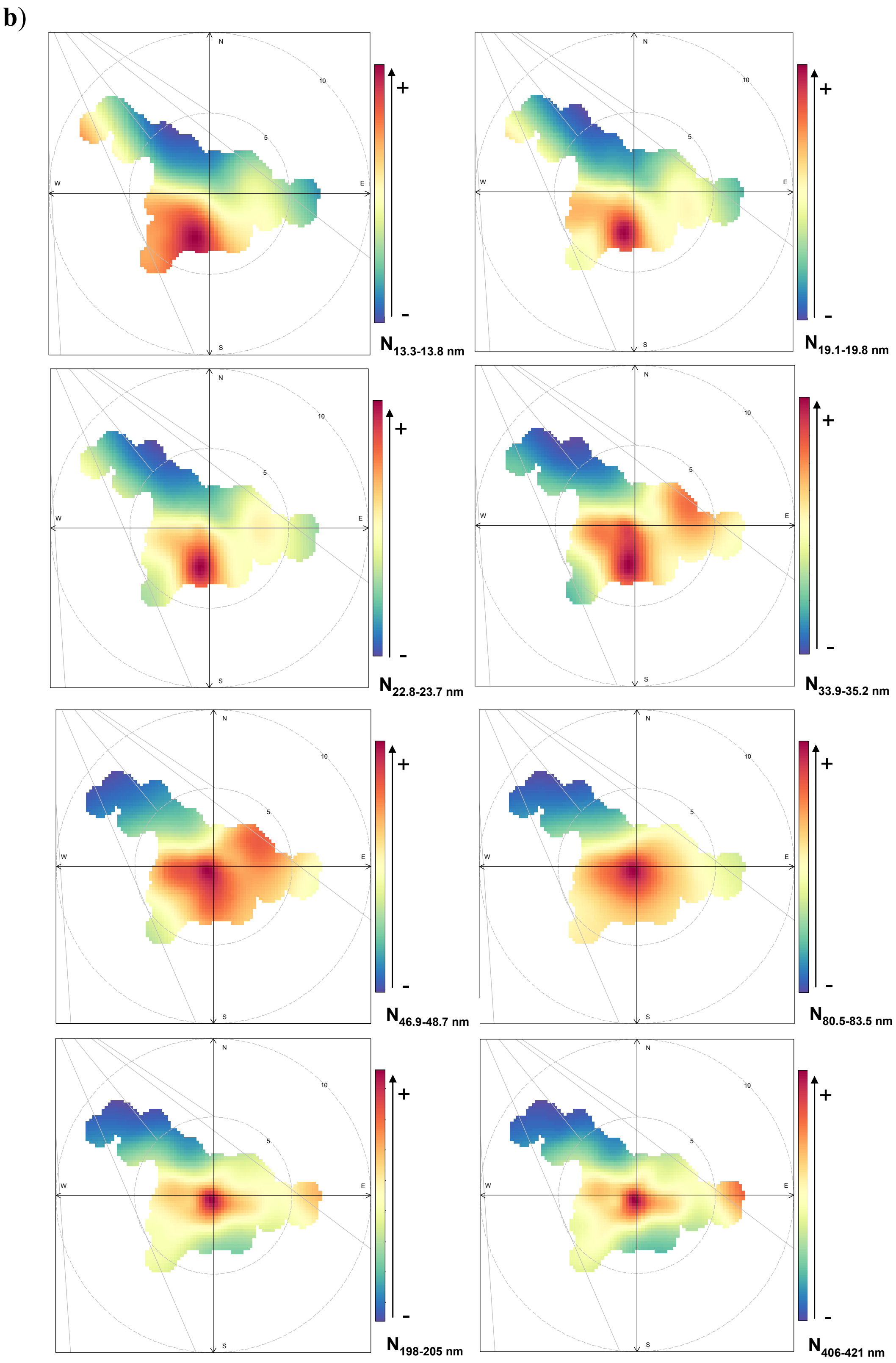

Figure 3.7. Continuation.

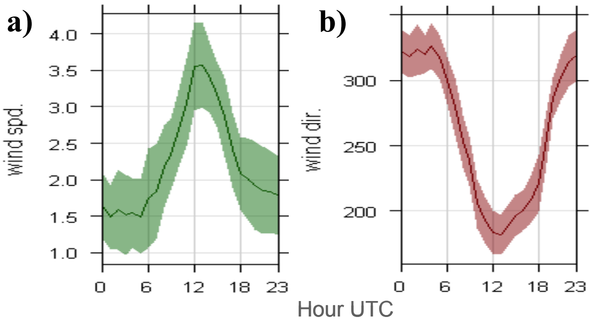

Figure 3.8. Time variation of wind components: a) Wind speed and b) Wind direction.

As regards PM concentrations, an additional factor producing a $PM_{2.5-10}$ peak between 10:00-14:00 h UTC is detected (Figure 3.9). It is important to note that the midday peak observed in the Figure 3.5 referred to particle number concentration while this discussion focuses on particle mass. This peak is superimposed on the predictable and already documented daily patterns of the finer PM fraction that depend on traffic emissions (Querol et al., 2001; Pey et al., 2008; Pérez et al., 2008), and is almost exclusive to the $PM_{2.5-10}$ fraction, indicating that the fine particles are not affected by this emission source. This new daily maximum for the coarser PM fraction, which in Barcelona is mainly associated with traffic resuspension, was ascribed to the emissions from the large number of construction and demolition works in the metropolitan area in 2009. In the early part of that year there were around 300 new major work sites (Ajuntament de Barcelona, 2010). Maximum levels of these emissions are increased by the presence of sea breezes. As previously mentioned, these breezes are at their strongest around midday and transport the re-suspended mineral material from the city toward the monitoring site. Mean values of $PM_{2.5-10}$ at 12:00 h UTC were calculated and compared with the 24-h mean on a daily basis for each year from 2003 to 2009. The ratio between the hourly increase in coarse PM at midday with respect to the daily mean PM level (Table 3.2) attained a maximum in 2009 (63%), highlighting the impact of construction works on urban PM levels. When comparing the mean values corresponding to those of the period of the DAURE campaign (24 February to 27 March) for each year, 2009 again presents the maximum ratio (88.6%). Barcelona city council provided data about licenses for major construction and reform works to be done throughout the city on a specific period. The number of works to be carried out between the end of 2008 and 2009 (1314 licenses) was 20% higher than the average for the period 2004-2008 (1061).

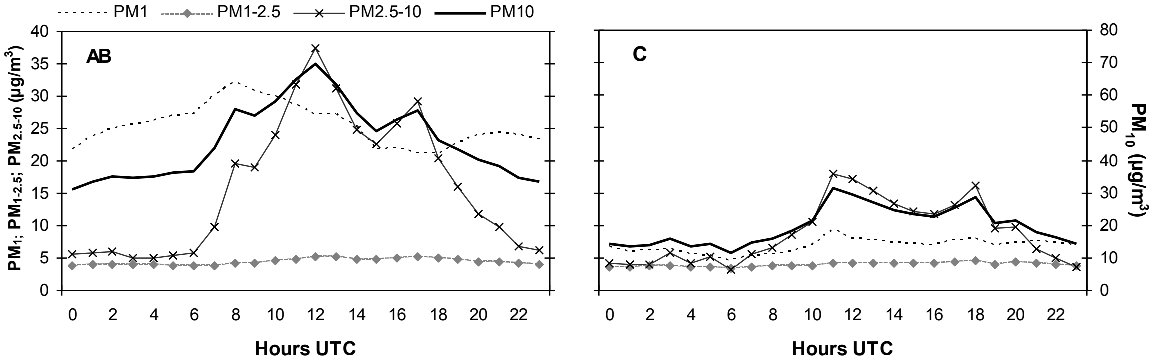

Figure 3.9. Averaged daily cycle of $PM_{2.5\text{-}10}$, $PM_{1\text{-}2.5}$ and PM_1 for the episodes AB and C.

Table 3.2. Ratio between the average hourly increase in coarse PM (µg m^{-3}) at midday with respect to the daily mean PM level from 2003 to 2009.

	2003	2004	2005	2006	2007	2008	2009
$PM_{10\text{-}2.5}$ (Daily average)	14.3	14.1	15.8	19.1	12.9	13.7	12.0
$^{12}PM_{10\text{-}2.5}$ (Average at 12:00 UTC)	17.6	16.9	23.4	25.2	17.2	18.4	19.5
$(PM_{10\text{-}2.5}-{}^{12}PM_{10\text{-}2.5})/PM_{10\text{-}2.5}$ (%)	23	20	48	32	34	34	63

Nevertheless, the mineral matter content of this source is similar to traffic resuspension, regional dust or Saharan dust, so it was not possible to attribute all the increase in $PM_{2.5\text{-}10}$ at midday to the construction/demolition source, but also to road dust. This should be considered a maximum value. However, low levels of traffic tracers (Ba, Sn, Sb, Cu) were registered during the midday peak, the opposite of what happened in the case of Ca and S (Figure 3.10), considered as the main tracers of construction works (Kim and Hopke, 2007; Karanasiou et al., 2009; Bernardoni et al., 2011), as these components can be ascribed to cement and gypsum used for construction activities as reported in Vecchi et al. (2009). Thus, it suggests that this midday increase is dominated by mineral matter from construction works emissions throughout the city. A more detailed description of metal hourly concentrations during the DAURE campaign is shown in Moreno et al. (2011).

Moreover, the study of the daily cycles during the different episodes as a function of wind direction allowed us to further confirm the construction/resuspension-related origin of this midday peak. The frequency of breeze circulations (originating from the 120-180º sector) was higher during AB episodes with the result that a higher contribution of construction works was expected during AB episodes. The analysis showed a major increase in $PM_{2.5-10}$ at midday with regard to the daily average during AB episodes (61%) with respect to C episodes (50%). This increase could not be ascribed to sea-salt aerosols given that the daily cycle of Cl did not show a peak at midday although the levels remained constantly high until the abatement of the breeze at 19:00 h UTC. This enabled us to verify the significant contribution of resuspension to the coarse PM levels due to changes in wind velocity and direction. Similar results were reported in earlier studies (Querol et al., 1998b; 2001, 2005; Harrison et al., 2001; Charron and Harrison, 2005), with coarse particle concentrations increasing with wind speed. However, it should be pointed out that other factors are influential in determining the magnitude of the resuspension effect. Given that meteorological data revealed no significant precipitations during the DAURE campaign, it was not possible to find a correlation with this parameter. Nevertheless, since Charron and Harrison (2005), Thorpe et al. (2007) and Amato et al. (2010) reported decreases in PM concentrations after rainfall, this long period of drought must have increased $PM_{2.5-10}$ levels.

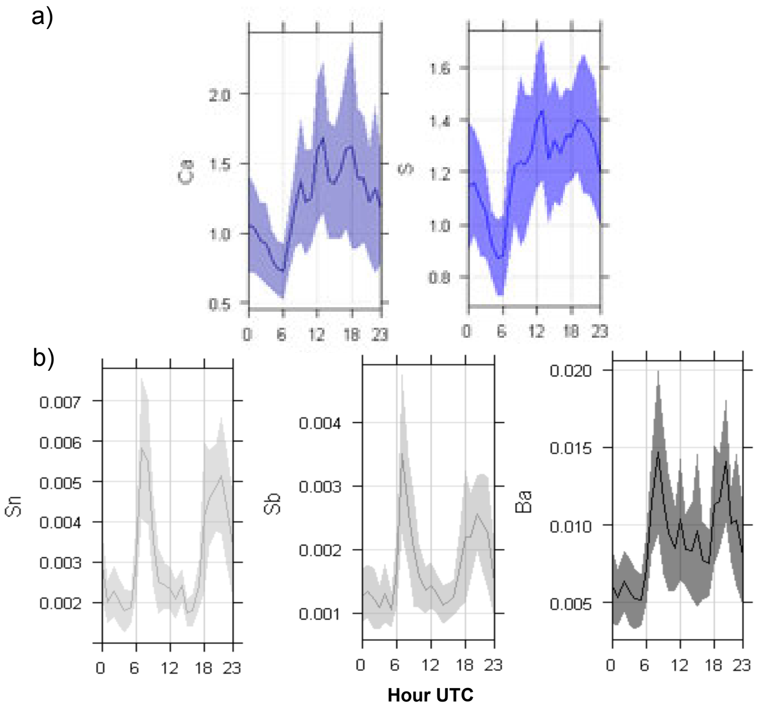

Figure 3.10. Time variation of: a) Construction-related tracers (Ca, S) and b) Traffic-related tracers (Sn, Sb, Ba).

Finally, concentrations of SO_2 reached a peak at times different from those of the other gaseous pollutants (described above). As shown in Figure 3.5b, SO_2 levels attain a maximum around 12:00 h UTC, coinciding with maximum sea breeze intensity. These breezes drive harbour emissions across the city, and thus SO_2 may be attributed to shipping emissions. No other major sources of SO_2 are present in the city. Hourly SO_2 maxima coincided with the noon peak of N, suggesting that SO_2 from shipping could be a major contributor to the aforementioned nucleation episodes at midday. The correlation between hourly levels of potential precursor gases (NO_2, NO, SO_2) and the particle number concentration was tested to assess the potential contribution of these gases to the nucleation process. However, no high correlations were found in any of the cases. Levels of SO_2 on C days were close to the detection limit with the result that it was not possible to confirm the contribution of this precursor. During AB scenarios, SO_2 and N correlated well ($r^2=0.67$) when BC concentrations were below 2000 ng m^{-3}, since the occurrence of nucleation processes are inversely proportional to air pollution levels.

It may therefore be concluded that traffic emissions govern the diurnal cycle of the levels of Black Carbon and most of the gaseous pollutants. SO_2, on the other hand, peaks at midday as a result of harbour emissions reaching the city by means of sea breeze circulations. Variability of ultrafine particle number concentrations on an hourly basis is driven not only by road traffic exhaust primary and secondary particles but also by nucleation processes. The large number of active construction-demolition sites during the sampling period in addition to resuspension of road dust constitutes the major determinants in the daily cycle of coarse particles ($PM_{2.5-10}$).

3.2.4. Secondary aerosol formation

In order to understand the sources and processes contributing to the variability of primary and potentially secondary particles, particle number concentration data were analysed using the methodology described by Rodriguez and Cuevas (2007), where:

$$N1=S1*BC \qquad (1)$$

$$N2= N-N1 \qquad (2)$$

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 (7-9 h UTC). This slope is about 4.8 particles ng^{-1} BC, which is in the order of those obtained in other Spanish cities: 4.9 particles ng^{-1} BC in Santa Cruz de Tenerife (Rodriguez and Cuevas, 2007) and 6.9 particles ng^{-1} BC in the industrial city of Huelva (Fernández- Camacho et al., 2010)

Figure 3.11 shows the hourly averaged values of N1 and N2 for each day of the week. On average, minimum primary emissions of vehicle exhaust (N1) account for 60% of the total particle number during the DAURE campaign, whereas the remaining 40% represents secondary parts from gaseous precursors, primary parts from non-traffic sources, and/or particles inherited in the air mass (N2). A significant contribution by N2 is observed in the afternoon (14:00-17:00 h UTC; N1=38%, N2=62%), doubling the number of N1 in some cases. This results from 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 harbour emissions due to sea breeze circulations. At midday (12:00 h UTC), N2 accounts for 61% of the particle number, which contrasts with the results obtained for the morning rush hours (N1=63%, N2=37%) and night periods (N1=68%, N2=32%). Finally, at weekends the contribution from the N2 component is 54%, which resembles the values obtained for the midday hours on week days (61%). This contribution is mainly due to the lower levels of atmospheric pollutants.

The daily cycle of N1 and N2 particles was plotted for scenarios AB and C (Figure 3.11b). Results show higher contributions of the N2 component during C days (71% of N2, as opposed to 42% during AB episodes), probably as a result of enhanced nucleation processes in a cleaner atmosphere. It should be pointed out that the daily cycle of minimum primary emissions of vehicle exhaust, which is clearly visible in Figure 3.11a and b for AB scenarios and coincides with rush hour traffic emissions, is not observed for C scenarios. This might be ascribed to the continuous air mass renewal produced by advective conditions. Moreover, the air mass advection inhibits the development of sea breeze circulations. Consequently, on C days the rush hour traffic peaks are not clearly observed. With regard to the rush hour peaks, the morning peak is mainly made up of N1, whereas a more marked contribution from N2 is observed in the evening peak. This is probably due to secondary aerosol formation during the day.

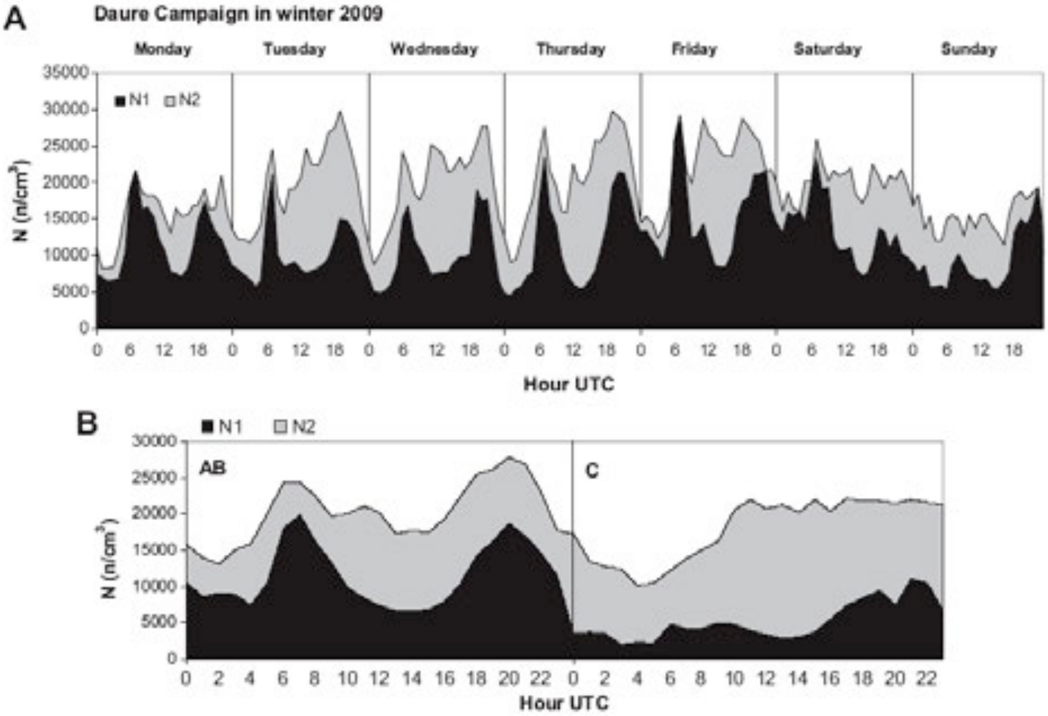

Figure 3.11. A) Mean hourly values of N1 and N2 for days of the week during DAURE campaign; B) Averaged daily cycle of N1 and N2 for scenarios AB and C during DAURE campaign. See text for discussion.

The correlation was investigated between N2 and SO_4^{2-} and NO_3^- on an hourly basis for each of the atmospheric scenarios (Figure 3.12). The different fractions of N2 (ultrafine) and SO_4^{2-} and NO_3^- ($PM_{2.5}$) was not expected to alter the analysis, since most of SO_4^{2-} and NO_3^- is found as ammonium sulphate and ammonium nitrate with a grain size lower than 2.5 mm during winter, as previously reported in Pérez et al. (2008) and Pey et al. (2009). An important difference in the concentrations of SO_4^{2-} and NO_3^- between both meteorological episodes should be noted. A high correlation was found between N2 and NO_3^- (r^2= 0.73) on C days, but not between N2 and SO_4^{2-}. It could be due to the fact that during this period, the breeze development was prevented by the intense Atlantic advection for most of the days and the SO_2 increase at midday was not detected, causing that the N daily cycle was simoultaneous to that of NO_2. However, it is important to highlight that the daily cycle of both NO_3^- and SO_4^{2-} levels during the campaign shows a peak at midday, which is especially pronounced for SO_4^{2-} during weekends (Figure 3.13). Although particle mass and particle number do not necessarily behave similarly, this analysis provides information on the chemical composition of N midday peak.

Correlations between N2 and SO_4^{2-} or NO_3^- are not high during AB days, but it should be noted that a negative slope is obtained in both cases. This could be due to the rapid transformation of SO_4^{2-} and NO_3^- into accumulation-mode particles by condensation and coagulation. These processes are caused by high concentrations of pollutants under stagnant conditions, giving rise a decrease in N.

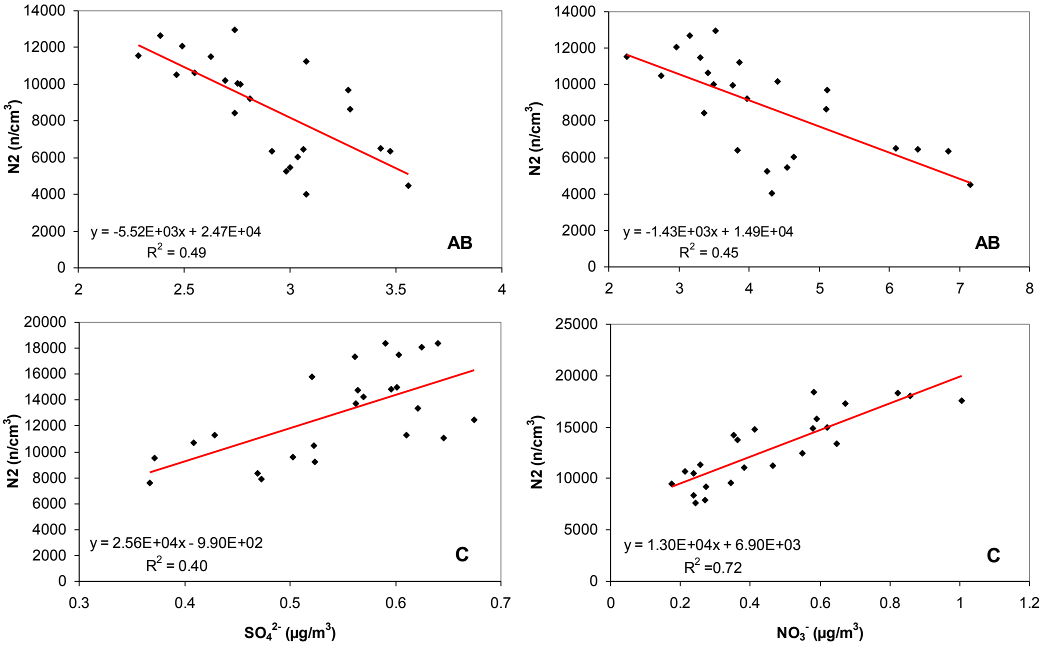

Figure 3.12. Correlations N2- SO_4^{2-} and N2- NO_3^- for scenarios AB and C. See text for discussion.

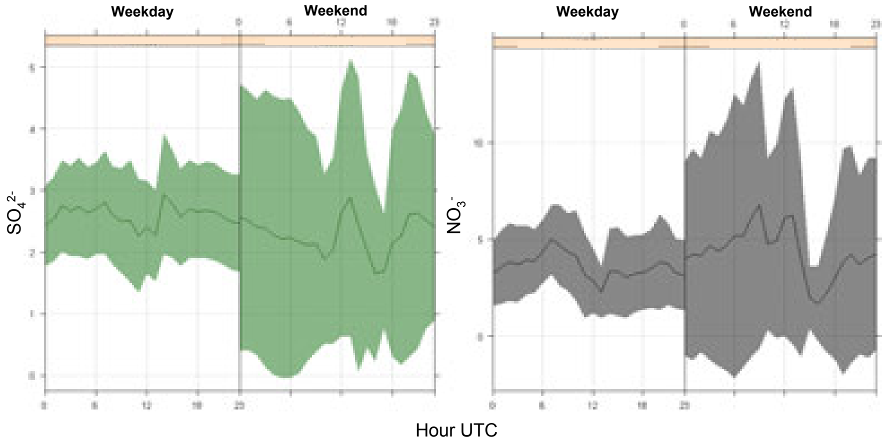

Figure 3.13. Time Variation of SO_4^{2-} and NO_3^- levels distinghising weekday and weekend for the whole DAURE campaign.

3.3. CONCLUSIONS

The sources and processes of atmospheric pollutants in a typical Mediterranean urban environment were evaluated. As expected, vehicular traffic proved to be the major emission source, governing the diurnal cycles of the fine aerosol fraction, Black Carbon and of most of the gaseous precursors (NOx and CO), with maximum levels coinciding with rush hours. Particle number concentrations also presented a third peak at midday, which was interpreted as secondary aerosol formation probably dominated by nucleation.

The study of the daily cycle of the coarse aerosol ($PM_{2.5-10}$) enabled us to identify the significant influence of an additional emission source, which was attributed to construction and demolition works. This source affected only the $PM_{2.5-10}$ fraction, the impact of which was strongly dependent on meteorological processes given that construction-derived dust seems to have been re-suspended and transported towards the study site by means of sea breeze circulations. In terms of mass, contributions from this emission source increased hourly $PM_{2.5-10}$ levels up to 63% with respect to the daily mean (an increase of 7.5 $\mu g\ m^{-3}$). As in many other cities across the world, new construction works were undertaken in order to lessen the impact of the economic crisis. One undesirable side effect of such activity is a significant increase in inhalable dust levels in the city.

Shipping and harbour emissions were also detected in the urban environment, using SO_2 levels as the main tracer. SO_2 concentrations peaked at midday, which coincided with the most intense sea breezes, suggesting harbour emissions as their main emission source.

Finally, secondary aerosol formation in the urban environment was found to be highly significant. The primary particles of vehicle exhaust (N1) showed a characteristic daily cycle and it accounted on average for 60% of the particle number during the monitoring campaign. The N2 fraction (secondary parts from gaseous precursors, primary parts from non-traffic sources, and/or particles inherited in the air mass) accounted for the remaining 40%, ranging from 37% during the morning rush hour to 61% at midday. Results show a high dependence of N2 on photochemical production of NO_3^- under advection conditions. During days of stagnation, coagulation and condensation probably give rise to negative correlations between N2 and concentrations of secondary compounds.

Source contributions were not calculated in this study but might provide interesting insights in future works with the dataset presented here.

This study confirms that the combination of PM_{10} and BC measurements in urban areas may constitute an accurate approach to monitor the traffic influence on air quality (BC), considering also the impact of other primary and secondary PM sources (PM_{10}). On the other hand, N in Barcelona is also an appropriate tracer for traffic effects, although it is shown to be very influenced by photochemistry.

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CHAPTER 4: New considerations for PM, Black Carbon and particle number concentration for air quality monitoring across different European cities

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4. NEW CONSIDERATIONS FOR PM, BLACK CARBON AND PARTICLE NUMBER CONCENTRATION ACROSS DIFFERENT EUROPEAN CITIES

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 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.

Key words: air quality, urban aerosols, nucleation, road traffic emissions

4.1. 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 them 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 and Liao, 2008). Epidemiological studies (Atkinson 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, 2011). 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., 2008b) 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, 2006).

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 (C) 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 et al. (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., 2004b; 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., 2011). 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., 2008; Gao et al., 2009; Cheung et al., 2011): (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., 2008; 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 SOx) 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, whereas VOCs account for more than 70% of the material for the particle growth (Weber et al., 1997; Boy et al., 2005).

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 southwestern 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., 2011). 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.

4.2. MONITORING SITES

In addition to the Torre Girona urban background site in Barcelona (BCN within this chapter), described in depth in the methodology chapter, five other European cities were selected for the purpose of this 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 4.1 and Table 4.2):

-. 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 25000 vehicles day^{-1}, and Marylebone road in London (UK, MR), with a traffic density of 80000 vehicles day^{-1}.

– 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.

Table 4.1. Main information about the monitoring sites selected for the study.

	Longitude	Latitude	Atitude (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°9'55'' W	51°31'96'' N	27	Urban traffic
Huelva (ES)	05°56'24'' W	3°15'21'' N	10	Urban industrial
Santa Cruz de Tenerife (ES)	16°18'33'' W	28°29'20'' N	52	Urban background

-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 4.2, 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 70Wm^{-2}, with values ranging from 5 to 760 Wm^{-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:

a) 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 (56º31'96''N; 00º09'55''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 80000 vehicles day^{-1} pass the site on six lanes with frequent congestion. Braking is frequent near the measurement site due to the presence of traffic lights 50m 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).

b) London, North Kensington, NK (urban background site): This is sited in the grounds of Sion Manning School in St Charles Square. Noth Kensington (51º31'16''N; 00º12'48''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.

-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 (46º57’03’’N; 07º26’27’’E; 536 m.a.s.l.). Attending to the typical meteorological feature, the mean annual solar radiation is 130 Wm^{-2} and it ranges from 15 Wm^{-2} in winter to 840 Wm^{-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 (20000–30000 vehicles day^{-1}). 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 4.2, Bern is characterized by a low proportion of diesel cars and heavy duty vehicles and a high proportion of motorbikes.

-Lugano, LUG (urban background site).

Lugano is a city with 55000 inhabitants and a total of 145000 people living in Lugano and the neighbouring community. The city lies at the edge of Lake Lugano at the southern foothills of the Alps (46º00’40’’N; 8º57’26’’E; 281m.a.s.l.) and is surrounded by three mountains with elevations of around 1000ma.s.l. As shown in Table 4.2, 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 Wm^{-2} on average, at midday this parameter is between 3 and 900 Wm^{-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 50m to the east is a busy urban road (Corso Elvezia), buildings protect the site from direct road traffic emissions towards all other wind directions.

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

Huelva is located in south-western Spain (37º15’00’’N; 06º57’00’’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 missions 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, NOx, 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 Wm^{-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.

-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 (28º29’20’’N; 16º18’33’’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 (Rodríguez 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 µgm^{-3} (Viana et al., 2002).

Table 4.2. 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 Transport.	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_mobiliaet.html.

[f] www.tiresia.ch.

[g] Oral communications from local councils.

4.3. INSTRUMENTATION

Data on the different instrumentation deployed at the different sites is summarized in Table 4.3. 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) (ThermoTM, model Carusso 5012) instrument calculates absorbance from particles deposited on the filter using measurements of both transmittance and reflectance at two different angles. As described in the methodology section, the absorbance is converted to the mass concentration of BC using a fixed mass absorption coefficient at 637 nm (Müller et al.,

2011) of 6.6 m^2 g^{-1} recommended by the manufacturer. Nevertheless, experimental results showed average absorption coefficients of 9.2m^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 24h 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 to the equation by Petzold and Schönlinner (2004) (1):

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

where σ_{ap} are the absorption coefficient measurements in Mm^{-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).

Table 4.3. Data from the air quality instrumentation working during the different sampling periods.

	Barcelona	Lugano	North Kensington	Bern	Marylebone	Huelva	Sta. Cruz de Tenerife
PM_{10} (µg/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.Grimm Labortechnik GmB & Co
Black Carbon (µg/m^3)	Multi-angle absorption photometer (MAAP Thermo ESM Andersen Instrument) with PM10 inlet	Multi-angle absorption photometer (MAAP Thermo ESM Andersen Instrument) with PM1 inlet	Magee AE-21 Aethalometer	Multi-angle absorption photometer (MAAP Thermo ESM Andersen Instrument) with PM1 inlet	Magee AE-21 Aethalometer	Multi-angle absorption photometer (MAAP Thermo ESM Andersen Instrument) with PM10 inlet	Multi-angle absorption photometer (MAAP Thermo ESM Andersen Instrument) with PM1 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 ($N_{2.5-1000}$)	CPC TSI model 3776 ($N_{2.5-1000}$)
SO_2 (µg/m^3)	UV fluorescence	UV fluorescence	UV fluorescence		UV fluorescence	UV fluorescence	UV fluorescence
NO , NO_2, NO_X (µg/m^3)	Chemiluminescence	Chemiluminescence	Chemiluminescence	Chemiluminescence	Chemiluminescence	Chemiluminescence	Chemiluminescence
CO (µg/m^3)	IR absorption	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

4.3. RESULTS AND DISCUSSION

4.3.1. 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 4.4 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 µgm^{-3}. As expected, the highest values (27–32 µgm^{-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 µgm^{-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 µgm^{-3} and decrease down to 3.5 µgm^{-3} in Bern, accordingly with the lower vehicle flow. On the other hand, HU (0.7 µgm^{-3}) and SCO (0.8 µgm^{-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 12000–18000 cm^{-3}, including the industrial site (with the highest levels), with this range increasing to 22000–28000 cm^{-3} at traffic sites due to the direct impact of primary exhaust emissions. N/BC ratios range from 6 to 9×10^{6} particles ng^{-1} BC, with the exception of MR (2.8×10^{6} particles ng^{-1} BC), HU (25×10^{6} particles ng^{-1} BC) and SCO (15×10^{6} particles ng^{-1} BC). The reasons behind these unusually low and high N/BC ratios will be discussed in the following sections.

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 (9.2 μg 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 NOx levels. Similar results have been reported in previous studies in nearby regions (Sandradewi et al., 2008b).

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 NOx 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 (80000 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 NOx/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.

Table 4.4. 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), with maximum values between stations 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} (µg/m^3)	30	7	60	12	23	7	40	12	18	6	30	7
Black Carbon (µg/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)	16847	5117	29449	6140	14945	9750	47562	2751	12134	5810	27295	792
SO_2 (µg/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 (µg/m^3)	58	27	163	17	25	18	80	4.4	46	22	112	13
NO (µg/m^3)	16	17	97	2	8	10	47	0.4	14	11	56	1.2
NO_2 (µg/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 (µg/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} (µg/m^3)	27	9	57	11	**32**	7	51	16
Black Carbon (µg/m^3)	3.5	1.3	7.1	1.3	**7.8**	2.7	14	2.5
Number of particles (n/cm^3)	**28032**	13650	93078	8888	22156	12910	58017	4753
SO_2 (µg/m^3)	-	-	-	-	6.7	2.7	13	1.6
NO_X (µg/m^3)	54	25	128	14	**233**	78	439	86
NO (µg/m^3)	27	19	89	5	**106**	27	178	49
NO_2 (µg/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 (µg/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} (µg/m^3)	23	9	58	6	21	7	34	7
Black Carbon (µg/m^3)	0.7	0.4	2.3	0.1	0.8	0.4	2.6	0.1
Number of particles (n/cm^3)	17918	13929	67949	1091	12008	7002	26294	1076
SO_2 (µg/m^3)	**9**	5	27	3.1	4	3	15	0.4
NO_X (µg/m^3)	32	20	136	4.3	13	7	39	0.2
NO (µg/m^3)	7	5	30	0.4	7	4	21	0.1
NO_2 (µg/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 (µg/m^3)	**61**	22	107	24	27	7	79	11

Table 4.4. Continuation.

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	**235**	167	158	143	90		188
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	**25598**	15010
N/SO_2	5265	**9341**	4494	-	3307	1948	3431
NO_2/NOx	0.7	0.7	**0.8**	0.4	0.5	0.7	0.5
NOx/CO	144	82	153	109	333	-	88

4.3.2. Temporal variability of atmospheric pollutants

Figure 4.1a shows the 2009 average daily cycle of gaseous pollutants for each site. For all sites levels of NOx (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/NOx 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, NOx 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 NOx and CO is followed by levels of BC (Figure 4.1a 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 (Figure 4.1c). 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 Figure 4.1c). 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., 1998b; 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., 2011). 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 (Maricq et al., 2007, Wehner et al., 2009).

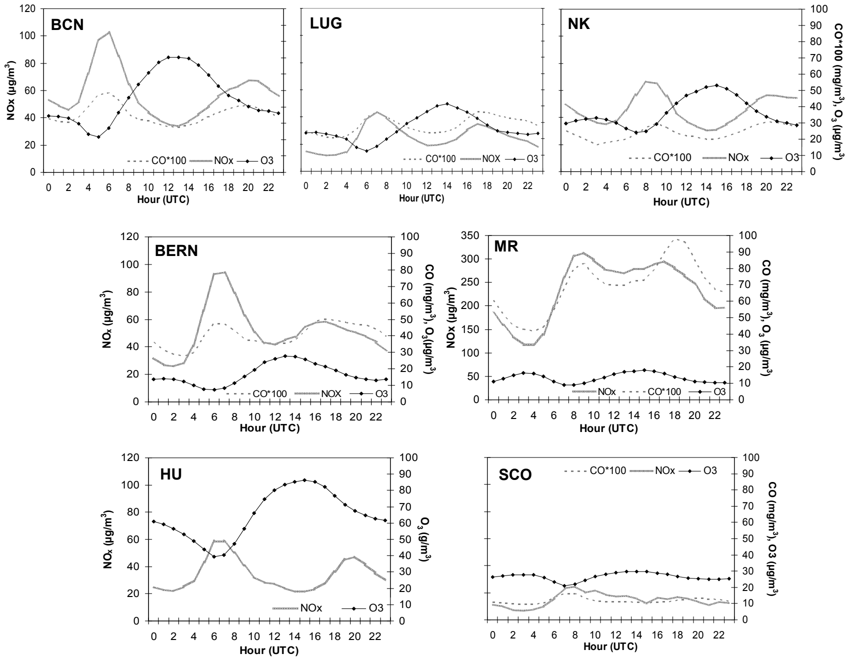
Furthermore, at BCN, HU and SCO, N shows a second peak at midday, simultaneously occurring with the BC decrease, confirming that this peak could not be a consequence of primary emissions from road traffic, but of secondary formation of particles by means of photochemical nucleation processes from gaseous 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 ($N_{5–20}$) (Figure 3.6). 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 (Figure 4.1d). 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).

a)



b)

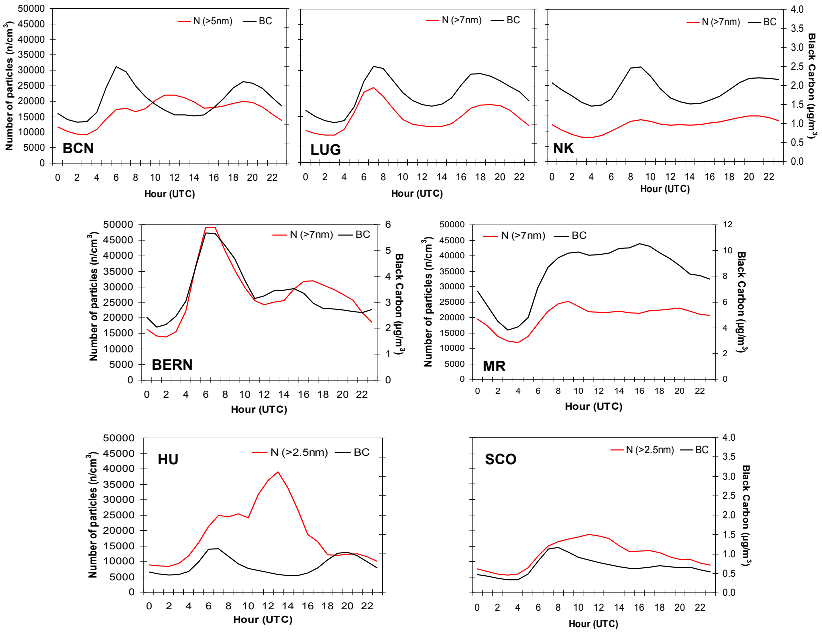


Figure 4.1. Daily cycles of a) gaseous pollutants concentrations (CO, NOx and O_3), b) Black Carbon (BC) and Number concentration (N), c) BC and PM_{10} levels and d) N and SO_2 levels for each monitoring site.

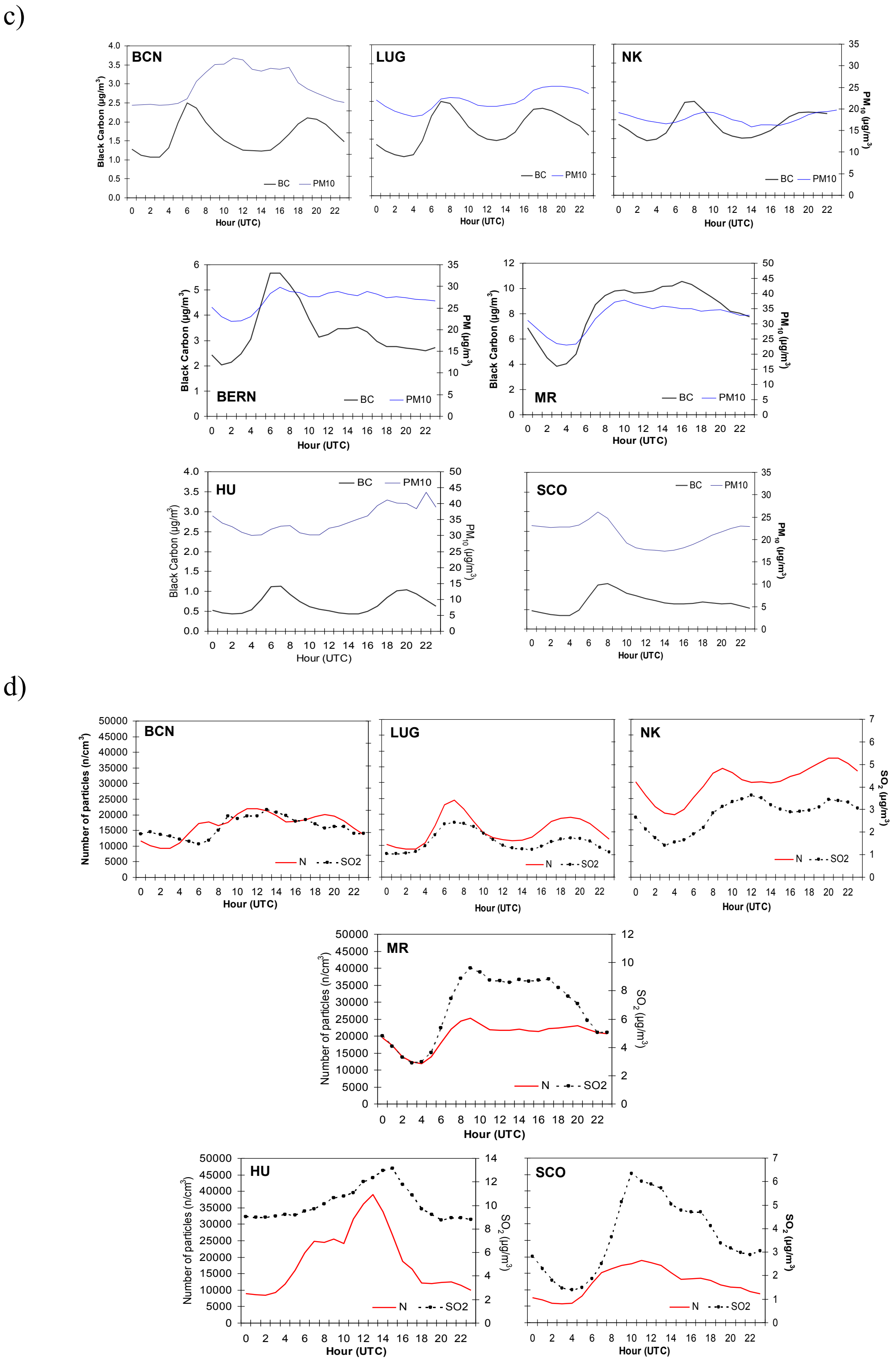


Figure 4.1. Continuation

On a weekly scale, the study of the daily evolution of N and BC for each day of the week and each station (Figure 4.2) 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 (Figure 4.3), 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 NOx concentrations follow the same seasonal trend described above for BC and N (Figure 4.4). However, NOx declines in summer are also evident in BCN. As expected, O_3 levels present an opposite tendency, increasing during the months with the highest solar radiation intensities (Figure 4.5). 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).

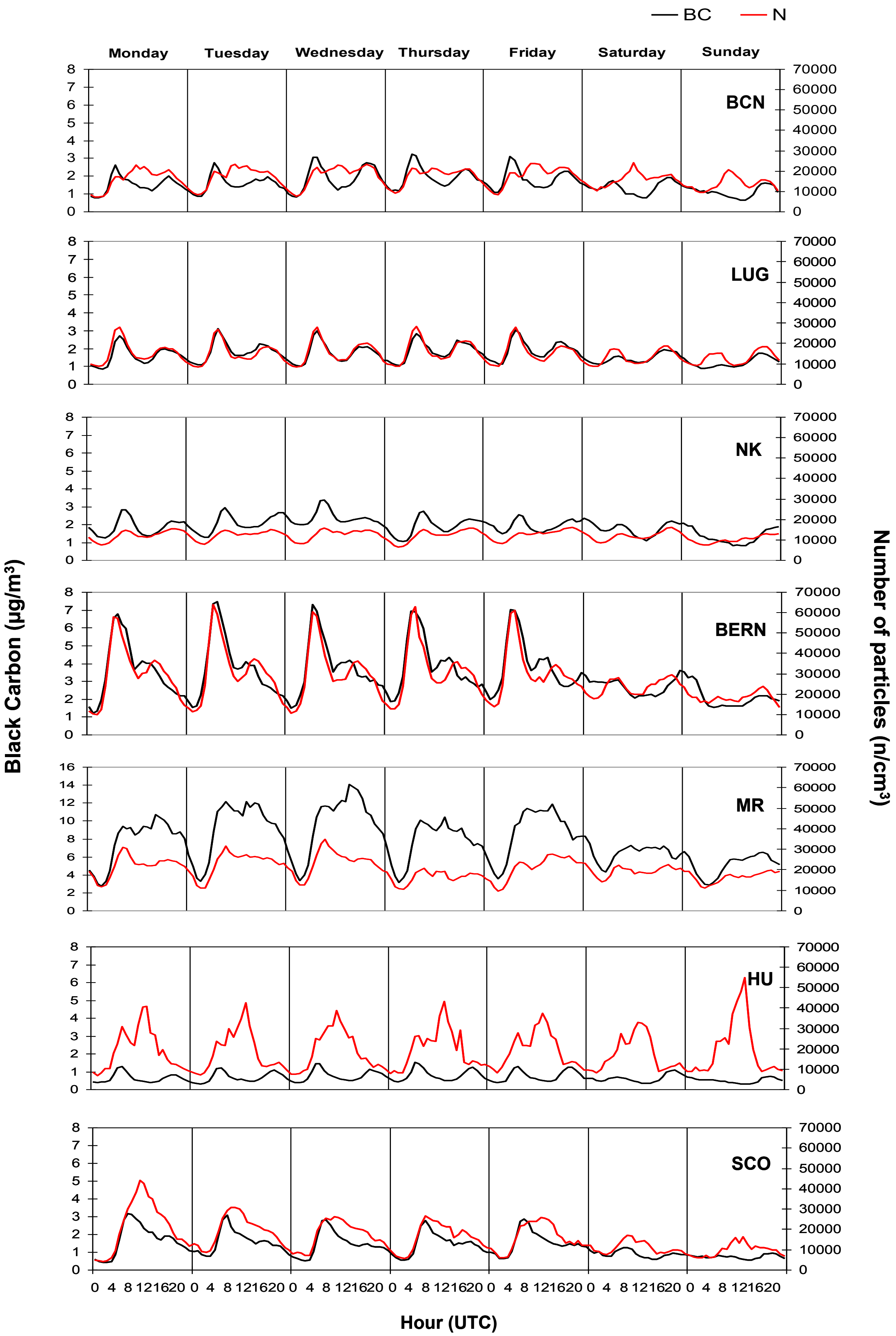


Figure 4.2. Daily cycle of BC and N for each day of the week.

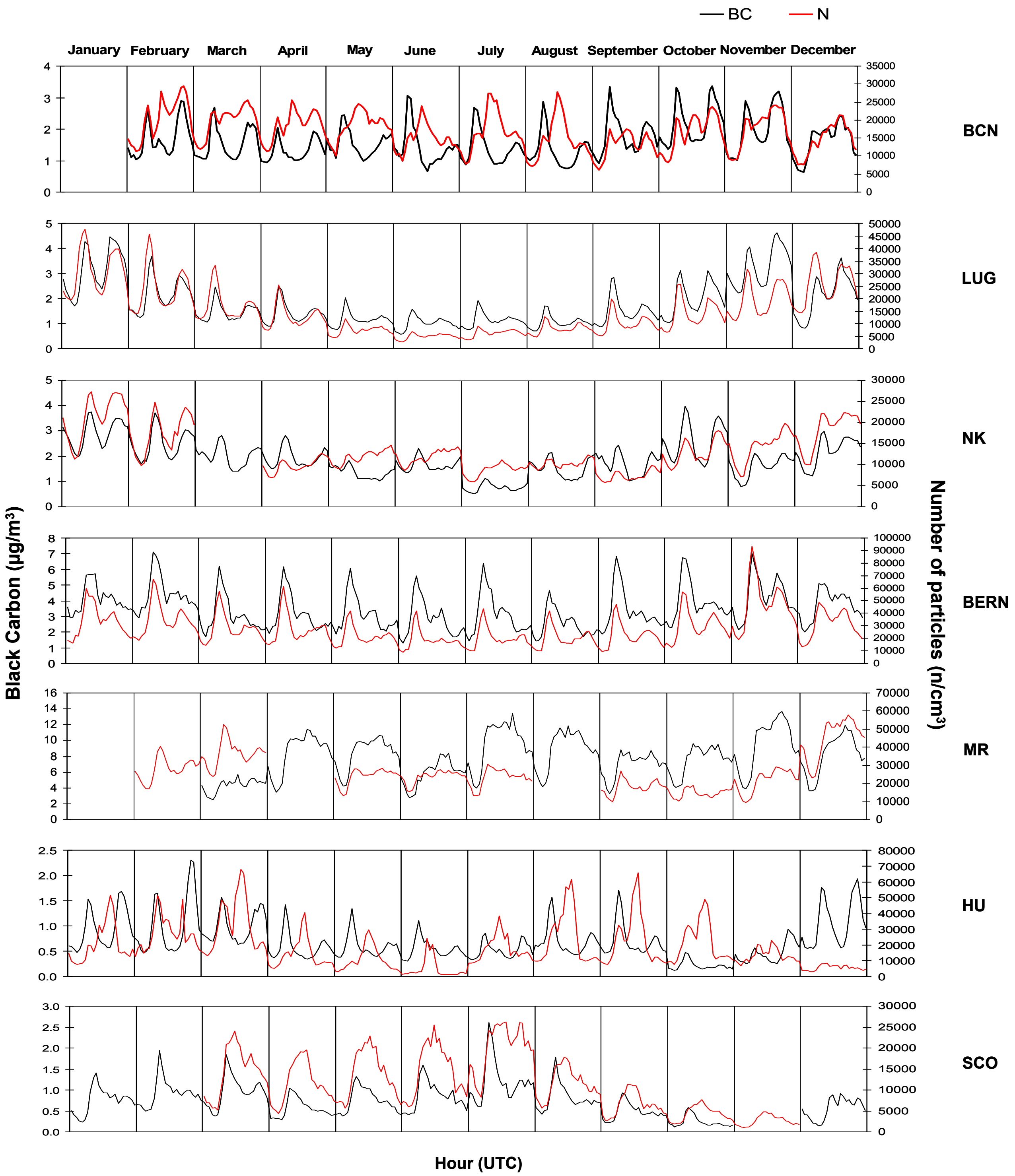


Figure 4.3. Daily cycle of BC and N for each month.

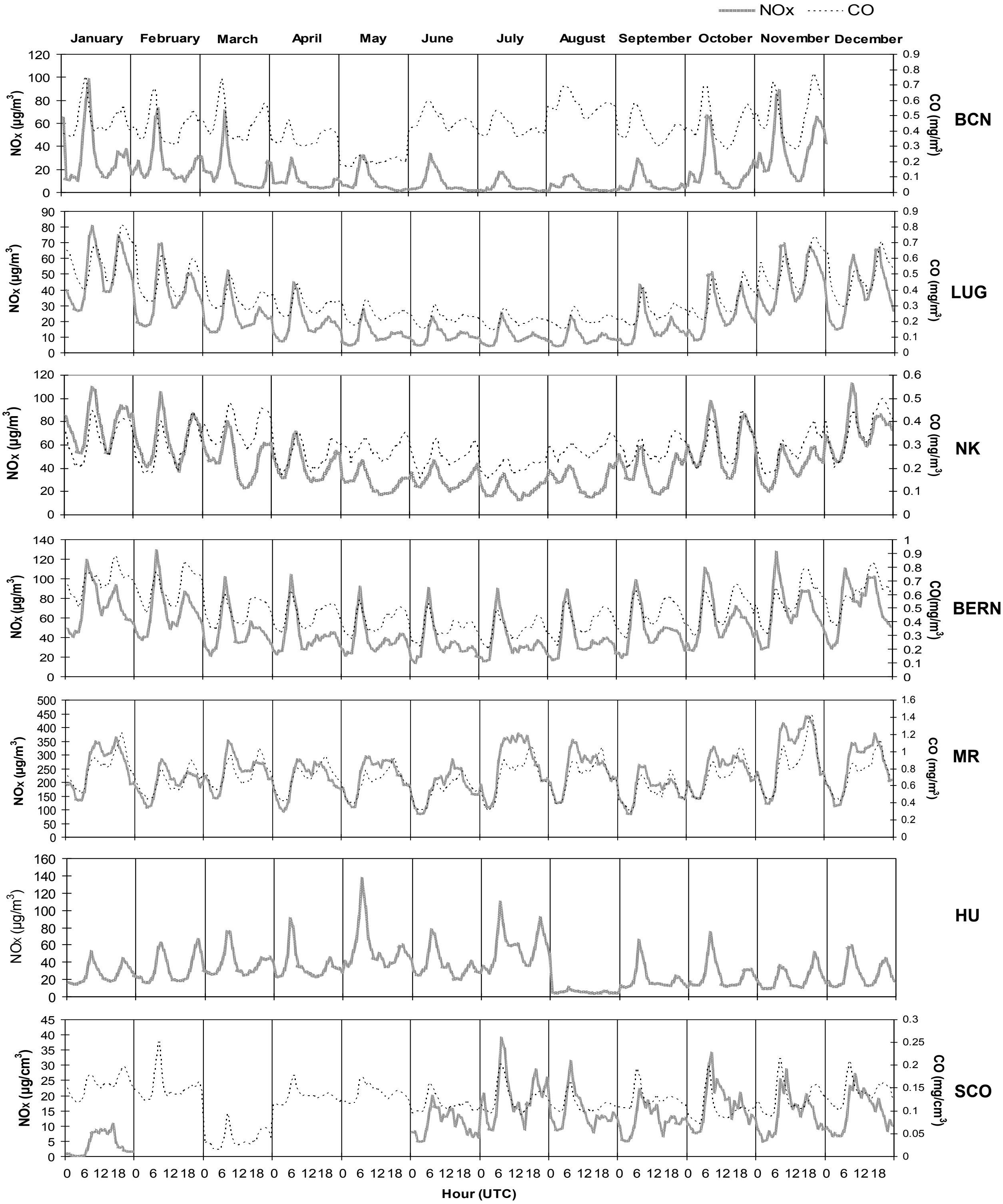


Figure 4.4. Daily cycle of NOx and CO for each month.

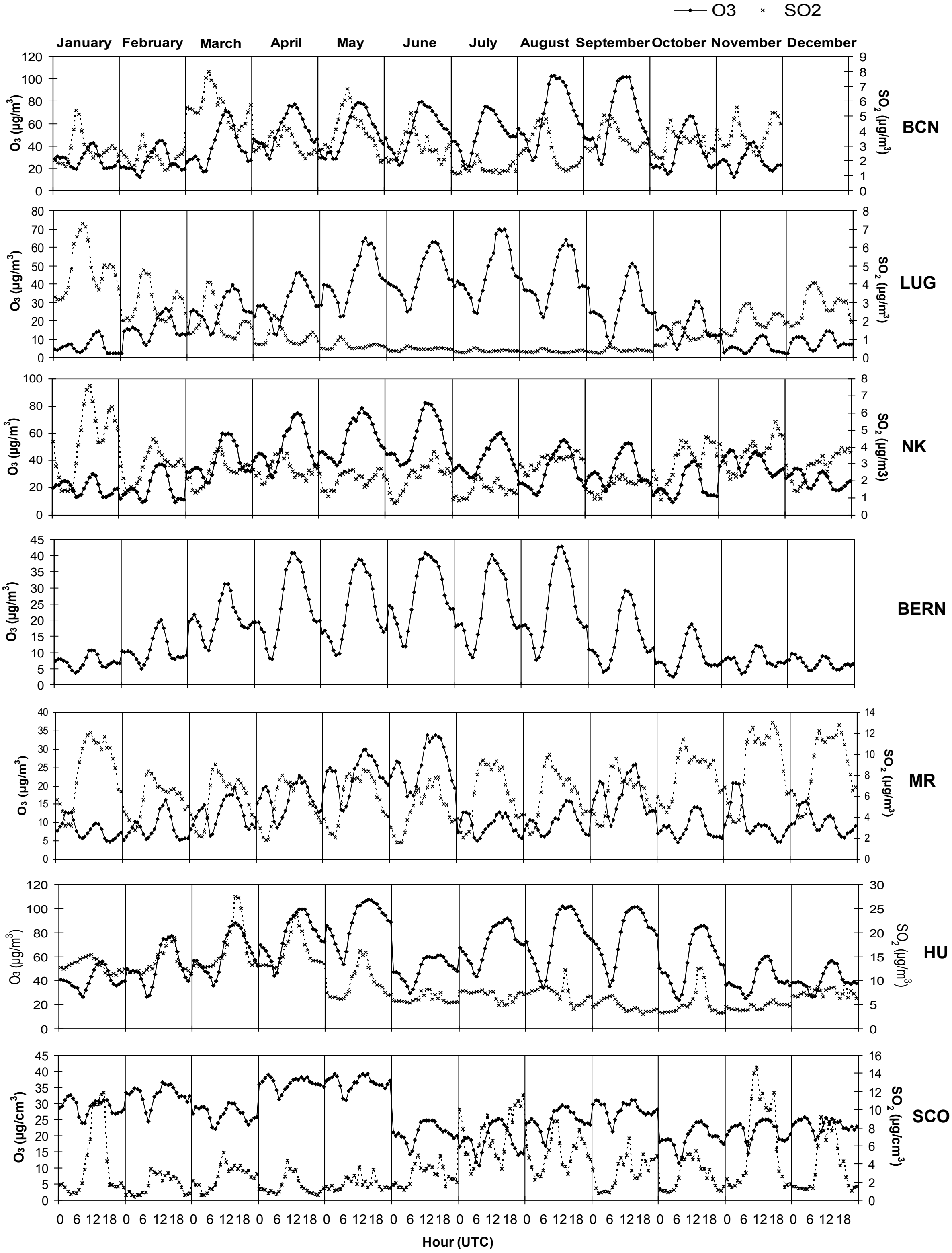


Figure 4.5. Daily cycle of O_3 and SO_2 for each month.

4.3.3. 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 Rodríguez 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 (Figure 4.6), specifically: 07:00–09:00, 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 11:00–14:00UTC 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 (Figure 4.6). 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.

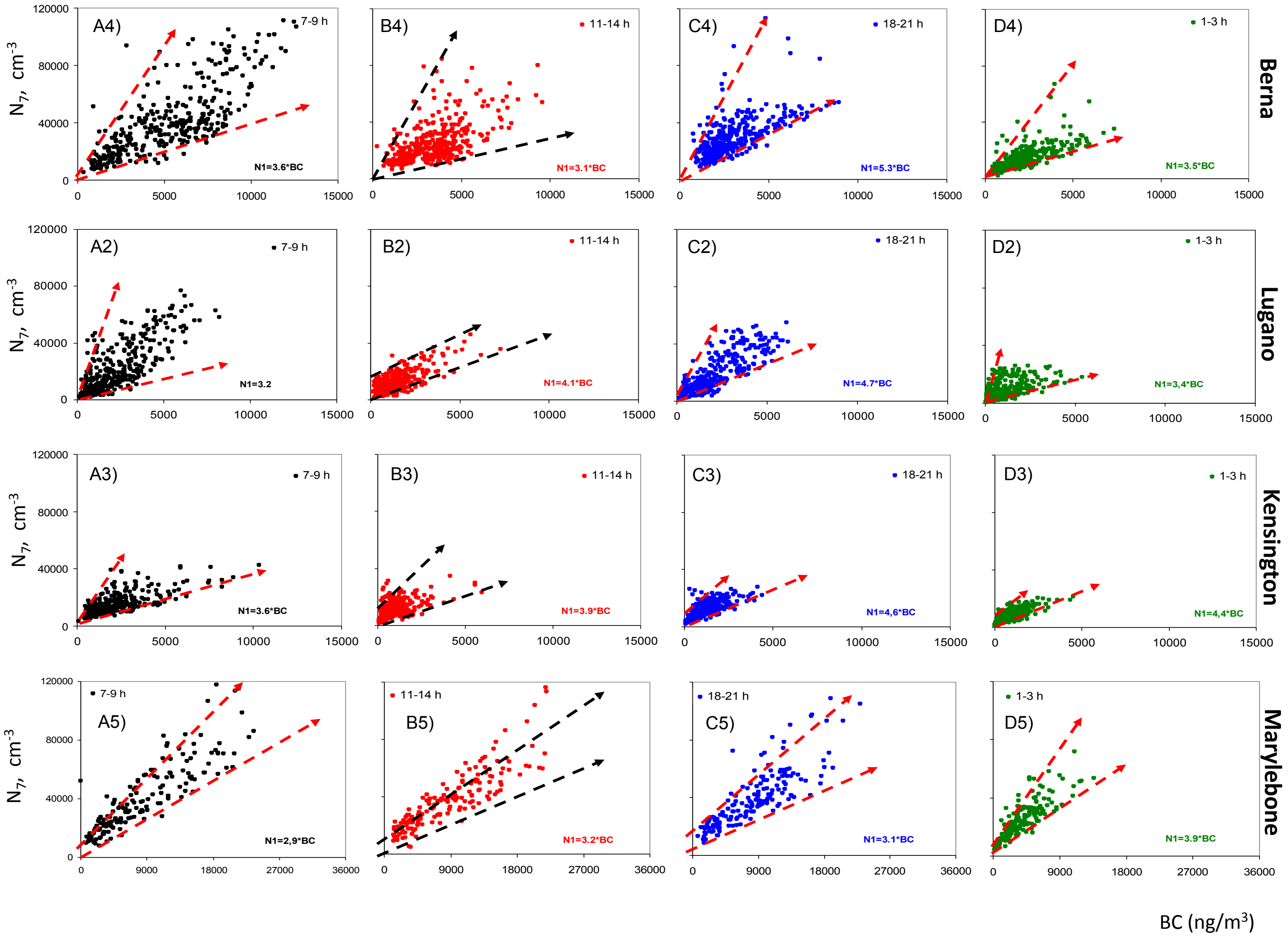


Figure 4.6. BC vs. N scatter plots for the different stations under study. 1:BCN; 2: LUG; 3: NK; 4: Bern; 5: MR; 6: HU; and 7: SCO.

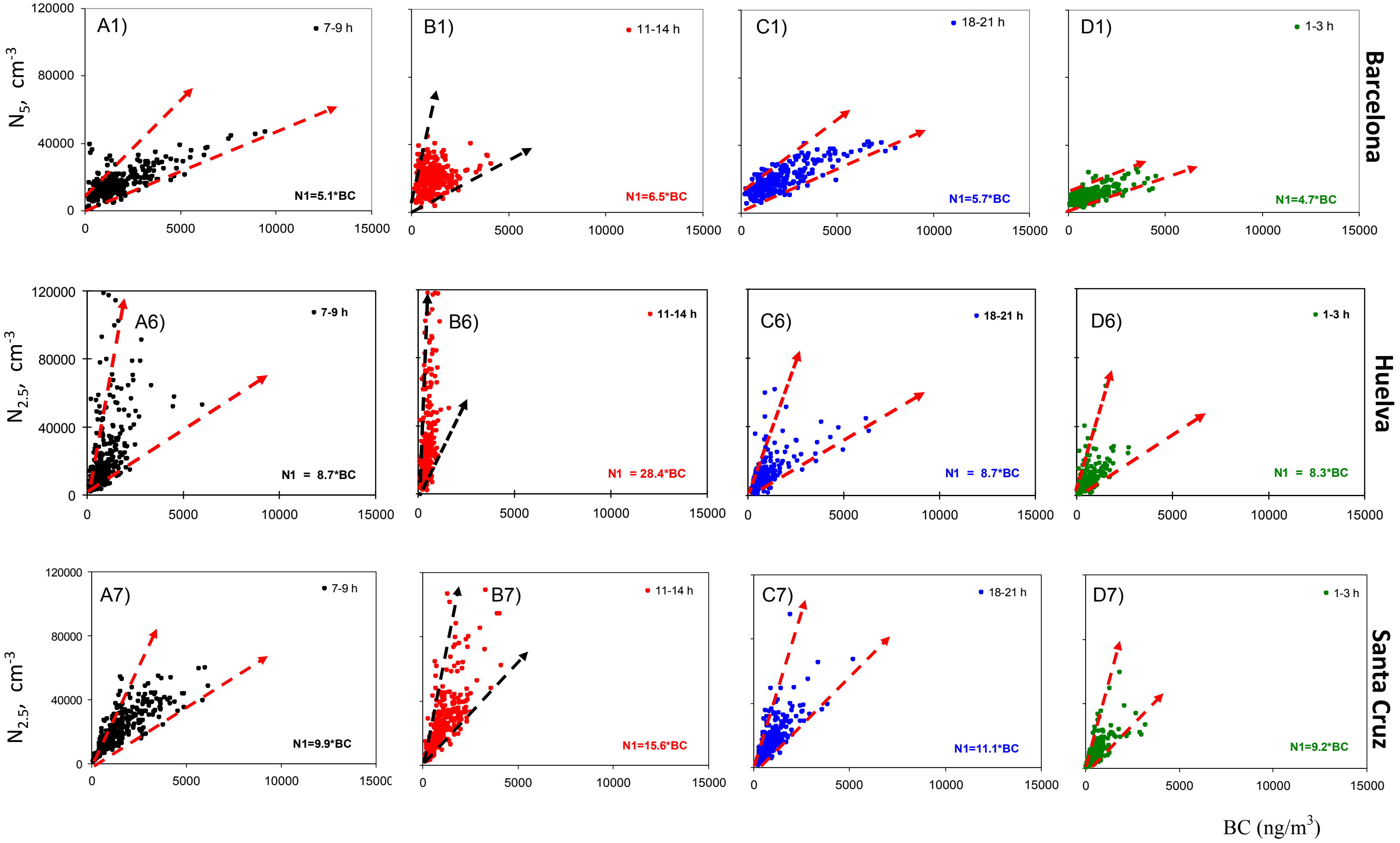


Figure 4.6. Continuation.

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 4.5). 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 between 3.1–4.1×10^6 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 3.1–5.3×10^6 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 4.7 shows the correlations between the mean annual hourly levels of N and BC for the above S1 ratios (Table 4.5) 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 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.

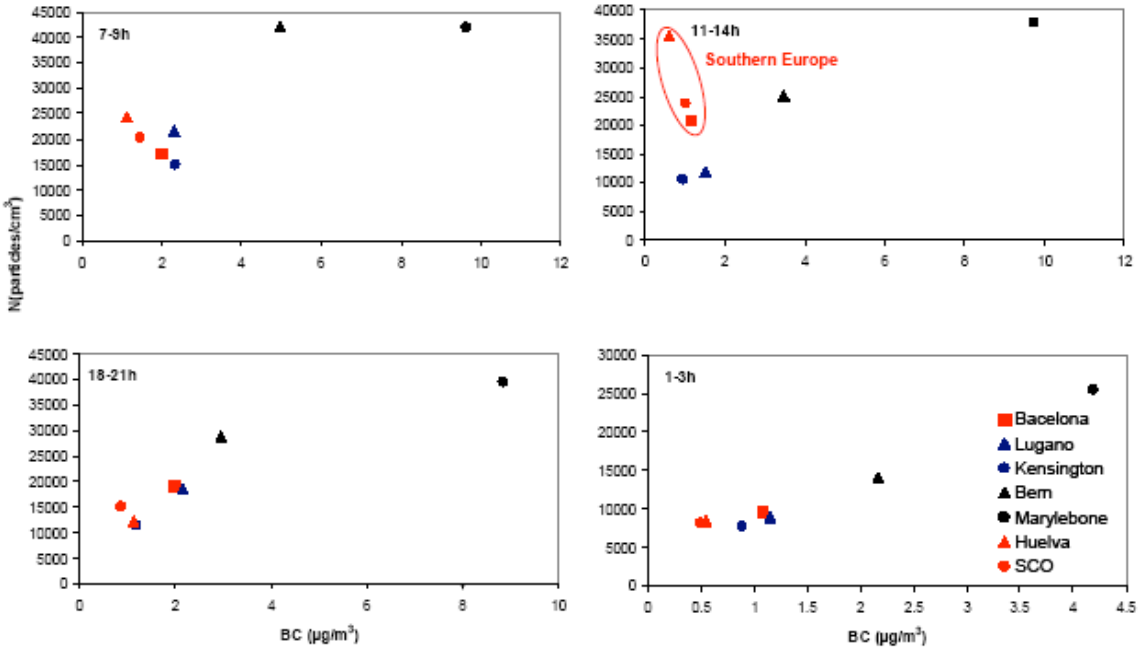


Figure 4.7. Correlation between the mean annual hourly levels of N and BC for the periods 07:00–09:00, 11:00–14:00, 18:00–21:00 and 01:00–03:00 (UTC) for the different study sites. SCO stands for Santa Cruz de Tenerife.

Table 4.5. Values of S1 and S2 representing the minimum and maximum BC/N ratio for each site.

	N(ncm^{-3})/BC(ngm^{-3})							
	S1				**S2**			
	7-9 h	**11-14 h**	**18-21 h**	**1-3 h**	**7-9 h**	**11-14 h**	**18-21 h**	**1-3 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

4.3.4. 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 defined by Rodríguez and Cuevas (2007), which has been previously described in chapter 3:

$N1=S1\times BC$ (2)

$N2=N-N1$, (3)

Values of S1 (expressed as 10^6 particles ng^{-1} BC) 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 4.8 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 layer (Figure 4.1d). This association between increases of N and power plant emissions has been observed in previous studies (Brock et al., 2002).

Table 4.6 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 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).

Table 4.6. Total averages 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	46
N2	54	61	46	55	22	62	53
N1 (11-14h UTC)	31	41	45	49	91	15	36
N2 (11-14h UTC)	69	59	55	51	9	85	64

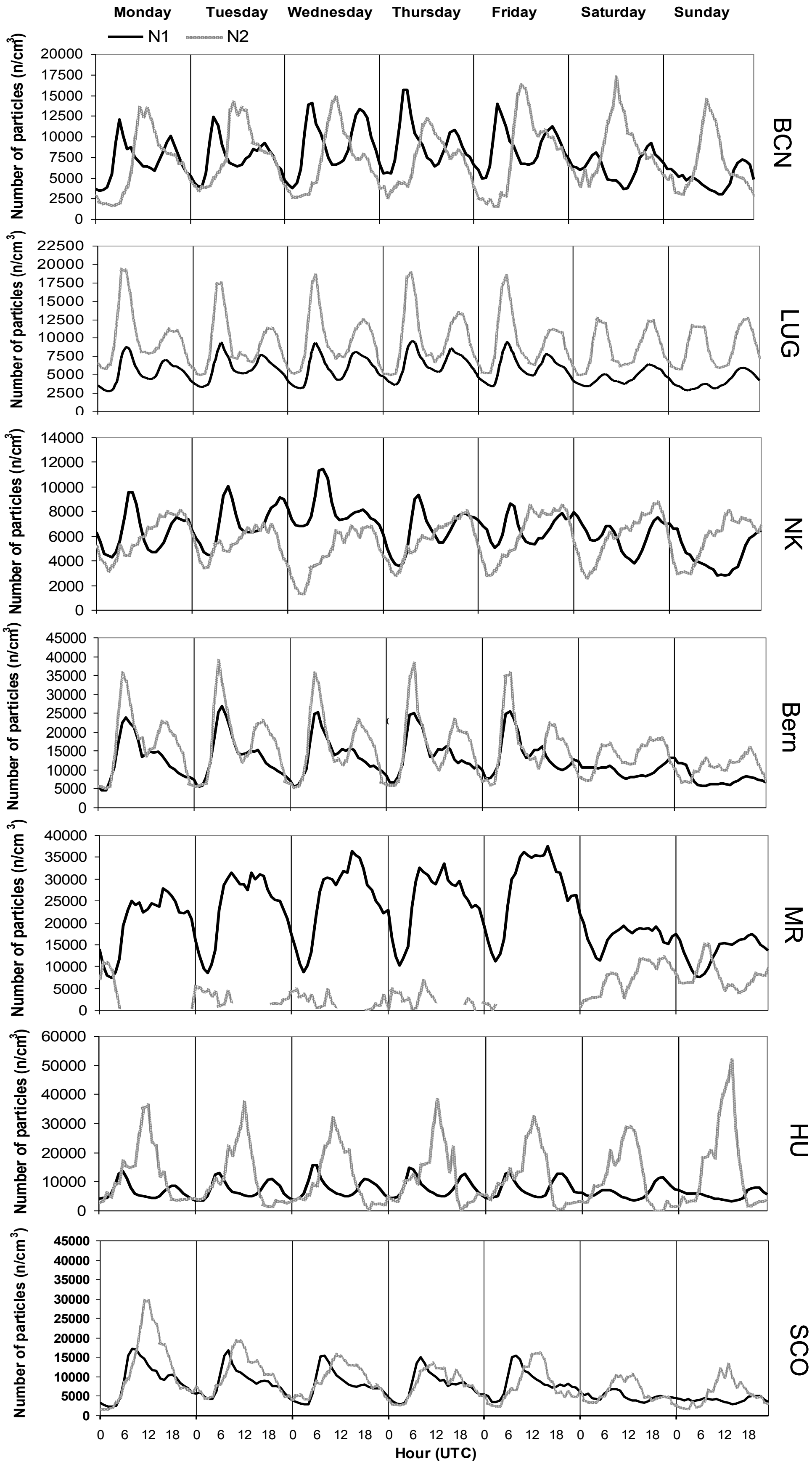


Figure 4.8. Daily cycle of N1 and N2 for each day of the week.

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* 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 (ρ =0.86), BCN (ρ =0.67) and SCO (ρ =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 high 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., 2008b).

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.

4.4. 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).

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CHAPTER 5: Urban NH_3 levels and sources in a Mediterranean environment

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5. URBAN NH_3 LEVELS AND SOURCES IN A MEDITERRANEAN ENVIRONMENT

ABSTRACT

Urban NH_3 concentrations were mapped in Barcelona by means of passive samplers (dosimeters). Average NH_3 levels were 9.5 µg m^{-3} in summer and 4.4 µg m^{-3} in winter, higher than those reported in other urban background sites in Europe, this being especially notable in summer. During this season, values were significantly higher at urban background than at traffic sites, probably indicating the impact of emissions from biological sources, such as humans, sewage systems and garbage containers. Thus, the volatilization of NH_3 from the aerosol phase seems to be significant enough during summer to dominate over traffic emissions. Conversely, in winter levels were higher at traffic sites, suggesting a contribution from vehicle emissions. Indeed, NH_3 levels decreased by 55% with increasing distance (50 m) to the direct emissions from traffic. A high correlation between NH_3 concentrations averaged for the different districts of the city and the number of waste containers per hm^2 was also obtained, highlighting the necessity for controlling and reducing the emissions from garbage collection systems. The urban topography of the Barcelona historical city centre, characterised by narrow streets with a high population density, seemed to exert a strong influence on NH_3 levels, with levels reaching up to 30 µg m^{-3} as a consequence of limited dispersion and ventilation conditions. The impact of the sewage system emissions was also detected with an increase of levels when measuring immediately above the source, even though further studies are required to evaluate the relevance of these emissions.

Keywords: urban ammonia, secondary inorganic aerosols, ammonium nitrate, passive samplers, ALPHA.

5.1. INTRODUCTION

Ammonia (NH_3) is the third most abundant nitrogen compound after nitrogen gas and nitrous oxide and the most important alkaline gas in the atmosphere (Seinfeld and Pandis, 1998). In the atmosphere, NH_3 reacts primarily with acidic species and neutralizes a substantial part of the acid produced by sulfur oxides (SOx), nitrogen oxides (NOx) and hydrochloric acid (HCl). These processes form secondary particulate matter including ammonium sulphate, ammonium nitrate and ammonium chloride, and as a result, ammonium (NH_4^+) is a major component of atmospheric aerosols (Asman et al., 1998). These NH_4^+ aerosols contribute significantly to aerosols mass ($PM_{2.5}$, PM_{10}) and have implications for human health (Brunekreef and Holgate, 2002; Verma et al., 2009). From a legislative perspective, they may be directly linked to the exceedance of the annual or daily limit values for PM_{10} in certain regions. The impact of ammonia and ammonium salts on the ecosystem has many effects, accounting for the acidification and eutrophication of the environment, the modification of the global radiative balance of the atmosphere and the reduction of atmospheric visibility, through light scattering (Sutton et al. 1993, IPCC, 2007; Erisman et al., 2008). Thus, because of the complex role of ammonia, the identification of its emission sources is a significant task in the field of atmospheric pollution. Despite this, there are large uncertainties in the magnitude of ammonia emissions, mainly due to a paucity of ground-based observations and an absence of atmospheric measurements (Bouwman et al., 1997; Asman et al., 1998; Galloway et al., 2008; Meng et al., 2011).

It is widely recognised that the main source of atmospheric ammonia is its volatilization from decomposing livestock waste, with the second major source being losses from vegetation and agricultural fields, particularly following the application of N fertilizers. As a whole, agriculture is estimated to contribute for around 95% to the total emission in Europe (EEA, 2011).

The estimation of non-agricultural NH_3 sources is an area of debate since the existing emission estimates are not sufficient to balance deposition and atmospheric transport (Sutton et al., 1995; Fowler et al., 1998; Erisman et al., 2008). In urban environments, these emissions include direct ammonia emissions from humans (including breath, sweat, infant excretion and cigarette smoking), from pets, biomass burning, sewage, garbage collection systems, household products and vehicle emissions. According to the technical report of 2011 of the European Environment Agency (EEA, 2011) about emission inventories, road transport is estimated to contribute with 2% to total ammonia emissions, industrial processes 1%, and waste decomposition 1%, the remaining percentage being attributable to agriculture from activities such as manure storage, slurry spreading and the use of synthetic nitrogenous fertilisers. Nevertheless, road traffic, industry or garbage emissions are very significant NH_3 sources from a local perspective in urban areas, as has been reported in previous studies (Sutton et al., 2000; Perrino et al., 2002). The EEA report shows a slow decrease of concentrations of this pollutant from 1990 to 2009, the rate of decline being almost constant over the last 10 years, in contrast to decreases of SOx, NOx or PM which are much higher.

Sutton et al. (2000) pointed to the transport sector as the main source of non-agricultural ammonia emissions (16%) in the UK, followed by sewage emissions (12%). The former is directly related to the type of vehicle fleet in the site under study, since 94% of transport emissions are due to gasoline cars with catalysts. In the US, EPA estimated the contribution of traffic of about 5% to the total ammonia emissions (Kean et al., 2009).

An increase of NH_3 emissions in urban environments due to the introduction of vehicles equipped with catalytic converters has been reported in the literature (Moeckli et al., 1996; Fraser and Cass, 1998). Gasoline vehicles equipped with catalytic converters generate ammonia through the reaction taking place in the converter between NO and H, which is produced particularly when the air/fuel ratio of the combustion is lower than the stoichiometric value (fuel rich engine). Kean et al. (2009) and Burgard et al. (2006) reported that the highest average ammonia emission rates were observed for 10-year-old vehicles. The adoption of selective catalytic reduction (SCR) by the addition of urea or ammonia to diesel exhaust to meet nitrogen oxide emission standards could be also resulting in elevated NH_3 emissions from traffic. To date, no significant regulatory effort has been made in Europe to control NH_3 emissions from motor vehicles. In Spain, a new regulation recently implemented in January 2011 (R.D. 102/2011), established the requirement to measure ambient ammonia levels at five rural background stations covering the country and in one traffic site in cities with more than 500000 inhabitants. In addition, it is important to note that the Critical Level of NH_3 in ecosystems was set to 8 $\mu g\ m^{-3}$ as an annual average, although recent studies reported important effects on vegetation when levels are above 3 $\mu g\ m^{-3}$ (Cape et al., 2009). The issues implicated in addressing the critical level and highlighted in the review articles have been summarised in the proceedings of a workshop held in Edinburgh in

December 2006 under the sponsorship of the United Nations Economic Commission for Europe (UNECE) (Cape et al., 2008; Sutton et al., 2008).

Studies on the characterization of ambient air levels and sources of NH_3 in European urban areas are scarce, with concentrations ranging from 2.3 (Thessaloniki, Greece) to 3.9 $\mu g\ m^{-3}$ (Münster, Germany) at urban background sites, while levels increase to 5 (Edinburgh, Scotland) or even 17 $\mu g\ m^{-3}$ (Rome, Italy) near traffic (see Table 5.1 and references therein). From a global perspective, the highest NH_3 levels were obtained in megacities in Mexico, India, Japan and China, reaching daily averaged concentrations of 24 $\mu g\ m^{-3}$ (reported in Beijing during summer).

Urban ammonia is strongly source dependent, and it is thus very variable in the urban-scale (Hellsten et al., 2008). A detailed spatial coverage has been reported to be more important than high time resolution (Asman et al., 1998; Hellsten et al., 2008). Consequently, sampling methods that can be implemented cheaply but covering many sites offer the best campaign strategies. In this context, the primary goal of our study was to use ammonia passive samplers (CEH ALPHA) covering a large area of the metropolitan region of Barcelona (NE Spain) in order to obtain an urban map of NH_3 concentrations during winter and summer periods, following the specifications detailed in the methodology section. In addition, we attempted to further identify the main sources and factors responsible for the higher concentrations of this pollutant registered in certain areas of the city. To this aim, source-specific monitoring campaigns were designed focusing on the impact of traffic, waste containers, sewage system and urban design/topography on urban NH_3 levels.

5.2. RESULTS AND DISCUSSION

5.2.1. ALPHA passive samplers

CEH ALPHA passive samplers have been previously validated against the reference DELTA (Denuder long-term atmospheric) method (UK National Ammonia Monitoring Network 2008 Annual Report). This study compared the annual empirical calibration for the passive samplers, based on their theoretical sampling rate (not including any membrane or boundary layer resistance). The annual calibration functions of ALPHA samplers show both high precision and constancy between years. This is very important, as it lends support for the detection of temporal and spatial trends in ammonia concentrations.

Figure 5.1 shows the comparison between ALPHA passive samplers and AiRRmonia measurements. Levels are 51±13% higher for AiRRmonia concentrations than for passive samplers, but both methodologies correlate (r^2=0.83). It must be considered within the interpretation of the passive samplers results, but it is worthwhile mentioning that none of these methods is considered as a reference methodology.

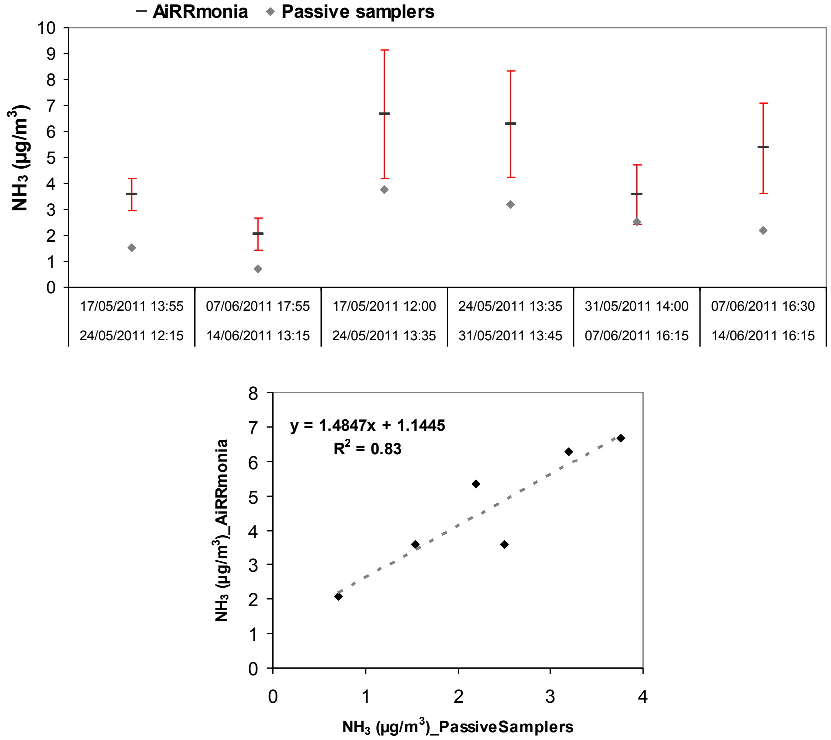

Figure 5.1. NH_3 concentrations obtained with the passive samplers versus those obtained with the AiRRmonia on-line measurements.

5.2.2. NH_3 levels and spatial variability in Barcelona

Table 5.1 summarizes ambient NH_3 concentrations reported in different studies indicating the background of the sampling site and the methodology employed for the collection. A comparison of these values with those obtained in the present study is not always very accurate because the measurement methods and/or the selected seasons for sampling differ widely among the different studies; however it is useful in order to evaluate the state of the NH_3 sources in Barcelona. The average concentration in the urban background sites in Barcelona during summer (10.6 µg m^{-3}) was higher than those reported in previous studies in American and European cities (Table 5.1 and references therein), with the exception of Croatia (45 µg m^{-3}), where the study was performed in a residential area with gardens being continuously fertilized. The annual average reported in a study carried out in Agra (India; 10.8 µg m^{-3}) is in the same order of magnitude as the concentrations obtained in the Barcelona urban sites in summer, although it is important to clarify that in Agra the selected site was close to agricultural fields. In winter, levels in Barcelona (3.9 µg m^{-3}) are similar to the annual concentration reported in Rome (3.7 µg m^{-3}) and of the winter values measured in New York (3.1 µg m^{-3}) but they are slightly higher than in the rest of studies considered here.

On the other hand, NH_3 concentrations in the traffic sites in winter (4.6 µg m^{-3}) are similar to those reported in Edinburgh (Scotland) in spring, while concentrations registered in Rome during May 2001-March 2002 were significantly higher than values during winter and summer, due to emissions from petrol-engine vehicles equipped with catalytic converters (Perrino et al., 2004). Levels at the regional site (1.9 µg m^{-3}) are similar to those reported from other countries, although lower than in some countries characterised by more intensive agricultural activity such as Taiwan or India. It is important to highlight the higher averaged levels obtained at the urban background and traffic sites of Barcelona compared with the regional site despite the elevated NH_3 emissions from agriculture activities in this region (National Inventory of Air Pollutant Emissions: 1990-2009; MAAMA, 2011).

The significant differences found between the urban background sites in Barcelona with other studies in European or American cities in summer, while these differences decrease in winter, suggest a significant impact of sources directly affected by temperature in the city. Numerous researchers have reported a seasonal cycle in ambient NH_3 concentrations (Robarge et al., 2002; Pryor et al., 2001; Lefer et al., 1999; Langford et al., 1992), with maximum concentrations occurring during warm months. This seasonal cycle in ambient concentrations is in agreement with the temperature dependence of aqueous-phase partitioning between NH_3 and NH_4^+, as well as the equilibrium between aqueous- and gas-phase NH_3 as predicted by Henry's law, which results in increasing ammonia emissions from animal manure, soils, and vegetation with increasing temperature (Asman et al., 1998; Ni, 1999). An increase in humidity was also found to increase ammonia concentrations and emissions (Nimmermark and Gustafsson, 2005). This model has been confirmed for natural and agricultural systems (Langford et al., 1992; Aneja et al., 2000; Ni et al., 2000; Harper et al., 2000; Roelle and Aneja, 2002).

Table 5.1. Ambient NH_3 concentrations summarized by study. “-“ means unknown data.

Study	Site	Background	Date	NH_3 (μg/m^3)	Methodology	Coating solution
Pio et al., 1991	Aveiro (Portugal)	Urban	August 1988-May 1989	3.1	The filter pack method	Potassium hydrogen sulphate
Yamamoto et al., 1995	Yokohama (Japan)	Urban	January 1987-December 1991	1.6-8	Bubbler with a teflon pre-filter	Boric acid
Buckhardt et al., 1998	Edinburgh (Scotlland)	Rural	September 1992-December 1992	1.4	Rotating wet annular denuder	Sodium hydrogen sulphate
Buijsman et al., 1998	8 sites in Netherlands	Agricultural	August 1992-July 1995	11	Continuos-flow denuder	Sodium hydrogen sulphate
McCulloch et al., 1998	Eastern North Carolina (USA)	Agricultural	September-December 1997	10.5	Annular denuder systerm (ADS)	Citric acid
McCurdy et al., 1999	Pittsburgh (USA)	Urban	June-September 1993	0.4-1.5	"Short-HEADS" annular denuder	Acidic sulphate
Parmar et al., 2001	Agra (India)	Urban	July-September and November-February (1997-1998)	10.8±2	Mist chamber technique	Sodium hydrogen sulphate
Pryor et al., 2001	Ohio river valley (USA)	Agricultural	April-May 1998 April-May 1999	0.7-1.2	Wet effluent diffusion denuders (WEDD)	Water
			January 1999 February 2000	0.3		
Perrino et al., 2002	Rome (Italy)	Urban traffic	May 2001-March 2002	17.2	Annular diffusion denuder	Phosphorous acid
		Rural	May 2001-March 2002	2.4		
		Urban	May 2001-March 2002	3.7		
Robarge et al., 2002	North Carolina (USA)	Agricultural	October 1998-September 1999	5.5±5.3	Annular denuder systerm (ADS)	Citric acid
Bari et al., 2003	New York (USA)	Urban	July 1999- June 2000	4	Annular denuder systerm (ADS)	Citric acid
			July-September 1999	6.1		
			January-March 2000	3.1		
			April-June 2000	5		
Carmichael et al., 2003	Shang dian Zhi (China)	Regional	September 1999- June 2001	1.9	IVL passive samplers	-
	Beijing (China)	Urban	September 1999- June 2001	<0.6		
	Shui-Li (Taiwan)	Regional	September 1999- June 2001	4.6		
	Chiang-Mai (Thailand)	Regional	September 1999- June 2001	1.3		
	Bangkok (Thailand)	Urban	September 1999- June 2001	<0.6		
	Dhangadi (Nepal)	Regional	September 1999- June 2001	14.6		
	Berhampur (India)	Regional	September 1999- June 2001	5.3		
	Bhubeneswar (India)	Regional	September 1999- June 2001	4.7		
	Tamanrasset (Algeria)	Regional	September 1999- June 2001	2.6		
	Isla Redonda (Argentina)	Regional	September 1999- June 2001	<0.6		
	Arembepe (Brasil)	Regional	September 1999- June 2001	<0.6		
Cape et al., 2004	Edinburgh (Scotland)	Urban traffic	April 2002	4.75	Passive samplers (CEH ALPHA)	Phosphorous acid
Pul et al., 2004	159 sites in Netherlands	Urban and rural	September 2000-September 2001	6.6	Passive samplers	Phosphorous acid
Walker et al., 2004	Clinton, NC (USA)	Urban	Winter 2000	2.6	Annular denuder systerm (ADS)	Citric acid
			Spring 2000	4.6		
			Sumer 2000	6.2		
			Fall 2000	2.8		
	Kinston, NC (USA)	Urban	Winter 2000	0.5		
			Spring 2000	3.9		
			Sumer 2000	2.7		
			Fall 2000	0.9		
	Morehead city, NC (USA)	Urban	Winter 2000	0.3		
			Spring 2000	0.4		
			Sumer 2000	0.7		
			Fall 2000	0.4		
Vogt et al., 2005	Münster (Germany)	Urban	May -June 2004	3.9	Continuous-flow wet denuder (AMANDA)	$NaHSO_4$
Anatolaki et al., 2007	Thessaloniki (Greece)	Urban	April 2002-March 2003	2.3	Annular denuder systerm (ADS)	Citric acid
Wilson et al., 2007	North Carolina (USA)	Agricultural	October 2003- December 2003	6.6	Passive sampler	Phosphorous acid
			January 2003- March 20004	5.3		
			April 2004- June 2004	7.2		
			July 2004- September 2004	11.1		
Alebic-Juretic, 2008	6 sites in Croatia	Urban industrial	Winter seasons 2000-2002	16.2	Nesslerization	-
			Spring seasons 2000-2002	12.2		
			Summer seasons 2000-2002	9.5		
			Fall seasons 2000-2002	15.8		
		Urban residential	Winter seasons 2000-2002	20.0		
			Spring seasons 2000-2002	30.8		
			Summer seasons 2000-2002	45.0		
			Fall seasons 2000-2002	20.0		
Hellsten et al., 2008	United Kingdom	31 cattle emissions sites	1996-2003	2.0	AENEID model	
		16 pig and poultry emissions sites	1996-2003	2.5		
		5 sheep emissions sites	1996-2003	0.9		
		3 fertilizers emissions sites	1996-2003	3.2		
		3 non-agricultural sites	1996-2003	1.8		
		18 mixed sites	1996-2003	1.9		
		9 rural background sites	1996-2003	0.3		
Fountoukis et al., 2008	Mexico city (Mexico)	Urban	March 2006	17.7	Quantum Laser (QCL) Spectrometer	-
Behera et al., 2010	Kanpur (India)	Urban	Winter 2007 and 2008	16.3	Chemiluminescence (Seres CV 2000 G)	-
			Summer 2007 and 2008	18.1		
Ianniello et al., 2010	Beijing (China)	Urban	August 2007	24.3	Annular diffusion denuder	Phosphorous acid
Meng et al., 2010	8 sites in China	Rural	October 2007- September 2008	4.5	Passive sampler (Ogawa)	-
Nowak et al., 2010	Atlanta (USA)	Urban	July-August 2002	1.25	CIMS techniques	-
Weijers et al., 2010	Schiedam (Holland)	Urban	Winter 2007 and 2008	2.2	Wet rotating denuder	
	Cabouw (Holland)	Rural	Winter 2007 and 2008	8.1		
This study	58 sites in Barcelona (Spain)	Urban traffic	July 2010	7.6	Passive sampler (CEH ALPHA)	Phosphorous acid
			January 2011	4.6		
		Urban	July 2010	10.6		
			January 2011	3.9		
		Regional	July 2010	1.9		

Table 5.2 shows the mean, the maximum and the minimum NH_3 concentrations and the standard deviation value at urban background sites as well as the NH_3 concentrations in each traffic sampling point indicating the corresponding number of vehicles per day. Average NH_3 levels at the urban background sites during summer (10.4 µg m^{-3}) were higher than those registered at the traffic ones (7.6 µg m^{-3}), with a range of values from 1.1 to 39.1 µg m^{-3} and from 3.5 to 17.9 µg m^{-3}, respectively. In winter differences were not so marked and mean levels reached 3.9 µg m^{-3} at urban background sites and 4.6 µg m^{-3} near traffic. The range of concentrations at urban sites was still very wide (0.8-8.9 µg m^{-3}), but it was more narrow near traffic (2.7-6.7 µg m^{-3}). This highlights the fact that the higher temperatures and solar radiation in summer will increase emission from biological sources in the city, such as humans, sewage and garbage collection systems, dominating over traffic emissions.

Table 5.2. Ammonia concentrations during the summer and winter campaigns in Barcelona: a) Urban background sites and b) Traffic sites.

a)

Urban background sites				
	Mean (µgm^{-3})	**Min (µgm^{-3})**	**Max (µgm^{-3})**	**SD (µgm^{-3})**
Summer	10.6	1.2	39.1	9.2
Winter	3.9	0.8	8.9	2.1

Table 5.2. Continuation.

b)

Urban traffic sites		
Vehicles/day	**NH_3 (µgm^{-3})-Summer**	**NH_3 (µgm^{-3})-Winter**
9400	8.9	3.9
60000	14.7	6.7
40000	9.2	4.1
12000	11.7	5.4
25000	16.3	5.6
16000	3.5	2.8
17000	7.5	5.1
17000	4	3
14000	3.8	3.6
20000	3.8	2.7
25000	17.9	6.4
97000	7.8	4.7
15000	3.7	3.2
8000	3.8	4.7
9000	4.5	4.1
50000	8.4	6.3
35000	4.5	4.1
35000	8.1	6.3
35000	6.2	4
35000	4.9	3.5
65000	8	5.6
9000	12.2	4.4
60000	8.8	4.7
6000	11.6	4
Mean (µgm^{-3})	**8.1**	**4.5**
Min (µgm^{-3})	**3.5**	**2.7**
Max (µgm^{-3})	**17.9**	**6.7**
SD (µgm^{-3})	**4.2**	**1.2**

In summer, the volatilization of NH_3 from the aerosol phase seems to be significant, given that whilst the solid ammonium sulphates are very stable, the reaction of ammonia and nitric acid is reversible and more temperature depended. As a result, the concentrations of ammonium nitrate are expected to be higher during the cold period of the year, something which has been observed in previous studies in Barcelona (Querol et al., 2001; Pérez, 2010). The seasonal variability of NH_4NO_3 and $(NH_4)_2SO_4$ has been studied in detail in an urban background site of Barcelona from 2003 to 2010 (Figure 5.2), observing average concentrations of NH_4NO_3 around 5-9 µg m^{-3} higher in winter than in summer. In the case of $(NH_4)_2SO_4$ concentrations are around 3-5 µg m^{-3} lower in winter than in summer due to the faster photochemical oxidation of SO_2 to SO_4^{2-} in summer. Thus, the higher NH_3 emissions and the favourable meteorological conditions for photochemical reactions enhanced the formation of stable $(NH_4)_2SO_4$ in summer, while the NH_4NO_3 concentrations are governed by volatilization and thus resulted in winter maxima.

When NH_3 levels were correlated for the same sampling locations in the different seasons (e.g., location 1 in winter vs. location 1 in summer), lower correlation coefficients were obtained for the urban background locations (r^2=0.28) than for the traffic ones (r^2=0.59). Sources differ from one area of the city to another and therefore temperature exerts a different impact on the NH_3 emissions in each area. This probably leads to a lower correlation at the urban background sites, due to the fact that NH_3 levels in the urban background sites are mostly dominated by biological sources (as opposed to the traffic sites, where vehicle emissions are the major source).

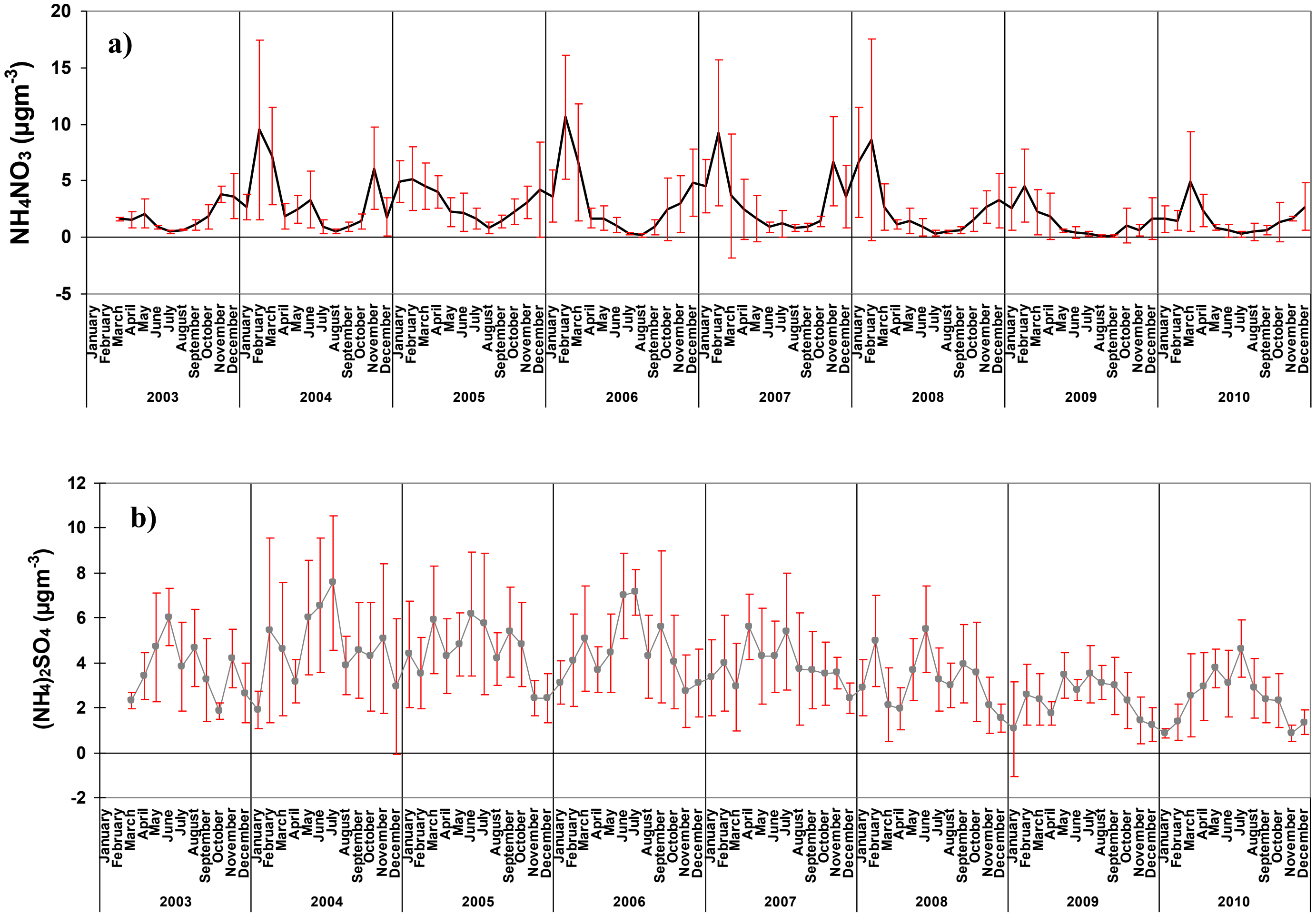

Figure 5.2. Monthly variability of NH_4NO_3 and $(NH_4)_2SO_4$ levels from 2003 to 2010. The data set has been obtained by means of chemical speciation of $PM_{2.5}$ samples collected on quartz micro fibre filters.

Figure 5.3 shows the spatial distribution of NH_3 concentrations during the summer and winter period. Attending to the urban background stations, higher levels are always found in the historical city centre. This area is characterized by a high population density (342 inhabitants hm^{-2} compared to 158 inhabitants hm^{-2} in the whole city) and an urban planning dominated by narrow streets which hinder the renewal of air masses. The combination of these factors is probably the responsible for the highest levels in that area. Indeed, levels in summer in the centre are 1.7 times higher than in sampling points with a number of vehicles/day above 20000.

a)

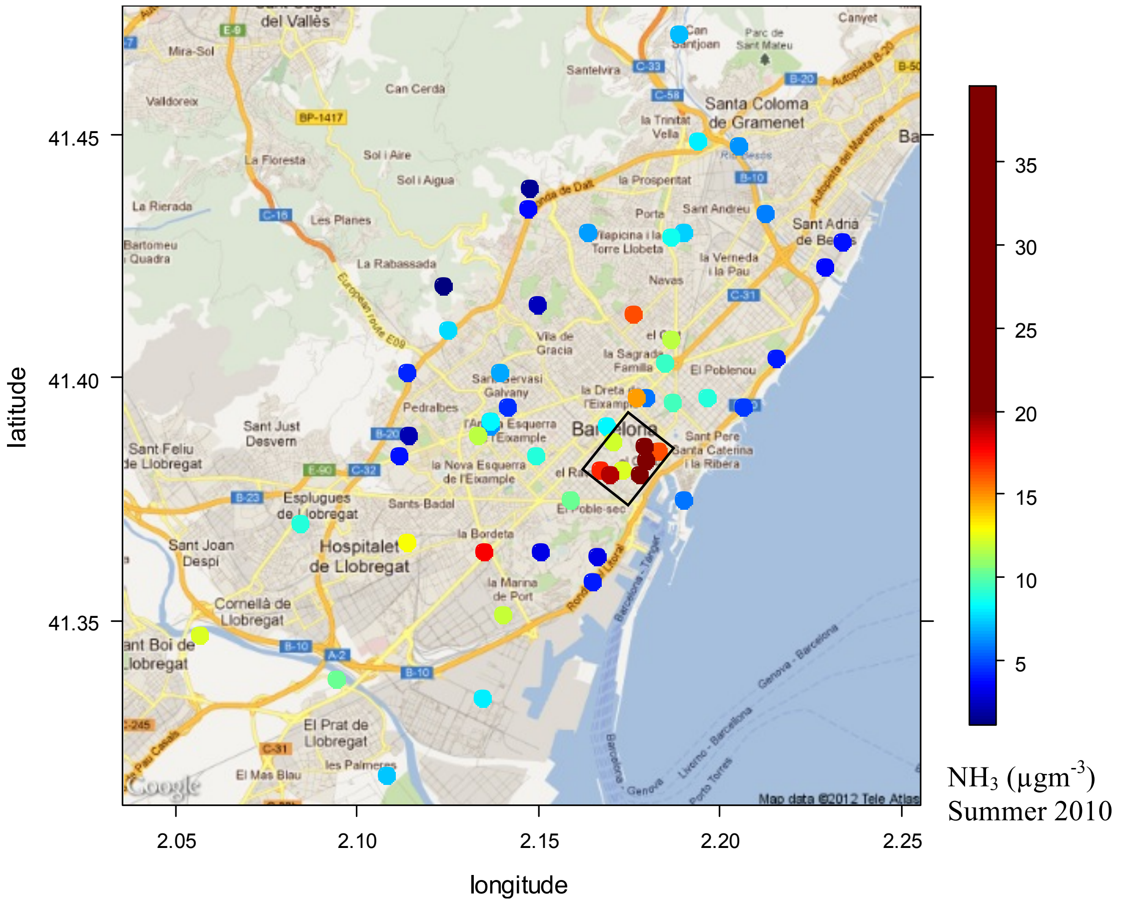

Figure 5.3. NH_3 concentrations distribution in the metropolitan area of Barcelona during summer 2010 (a) and winter 2011 (b). The black square indicates the location of the historical city centre.

b)

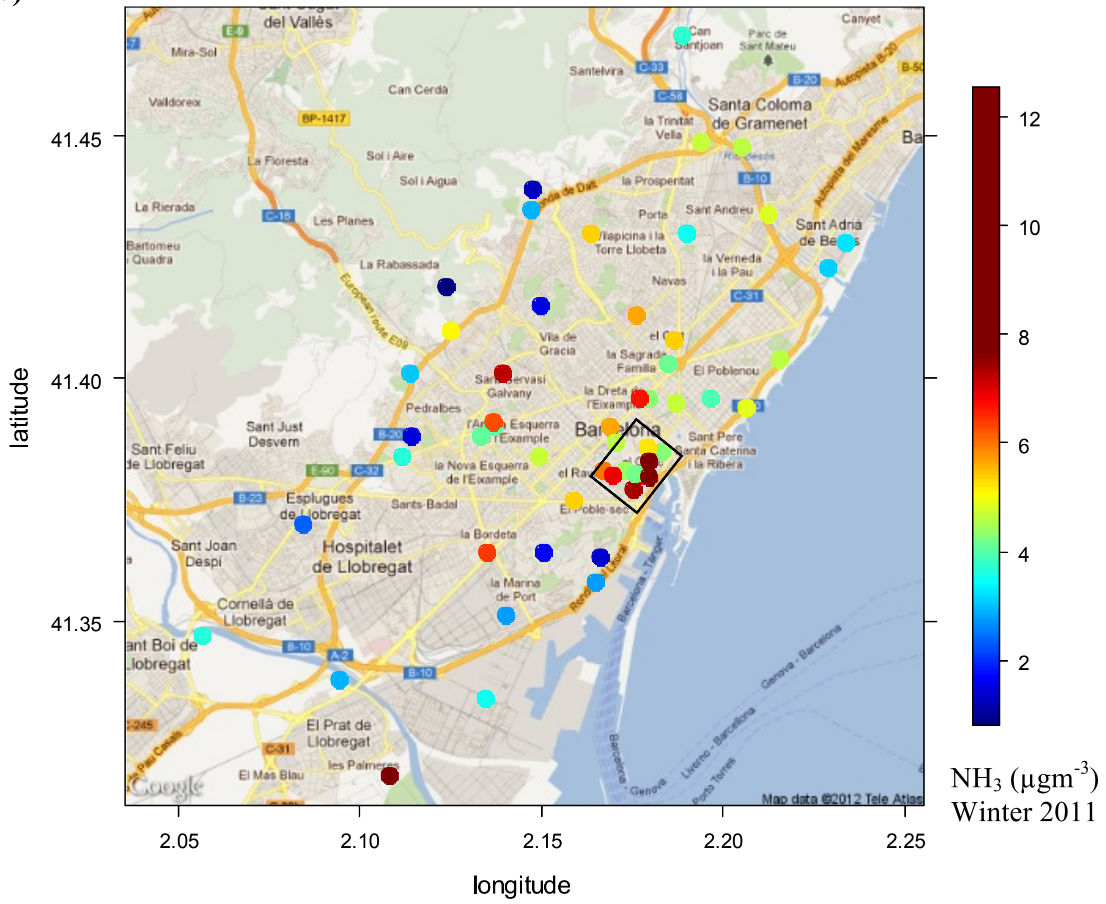

Figure 5.3. Continuation.

5.2.3. Secondary inorganic aerosol formation

Through the reactions with sulphuric and nitric acids, ammonia contributes to the formation of secondary particulate matter in the atmosphere.

Barcelona has been reported to be one of the cities with a higher contribution of nitrate, sulphate and ammonium salts to the total PM mass compared with other urban and industrial sites across Spain (Querol et al., 2008). Figure 5.4 shows the concentration of NH_3 and the contribution of secondary inorganic aerosols to the total $PM_{2.5}$ mass in Barcelona, the latter obtained during the summer and winter campaigns from 24-hour samples collected on quartz micro fibre filters every four days, as well as in other cities where data of NH_3 and water-soluble ions were available in literature. The comparison is not direct, given that measurement periods are not the same between data sets of NH_3 and water-soluble ions for some cities, the selected seasons for sampling differs among cities and the PM size fraction is not constant for all the studies (PM_{10} or $PM_{2.5}$). Nevertheless, it seems that the highest concentrations of secondary inorganic aerosols correspond with the highest levels of NH_3 (r^2=0.68). Therefore, emissions of this precursor gas together with favourable meteorological conditions (high temperature and relative humidity) seem to favour the formation of secondary inorganic particles and their contribution to the total PM mass. This would explain the higher NO_3^- levels registered in Barcelona with respect to other Spanish cities such as Madrid, despite the higher traffic volume in this city (935000 vehicles in Barcelona compared to 1925000 vehicles in Madrid; DGT, 2011).

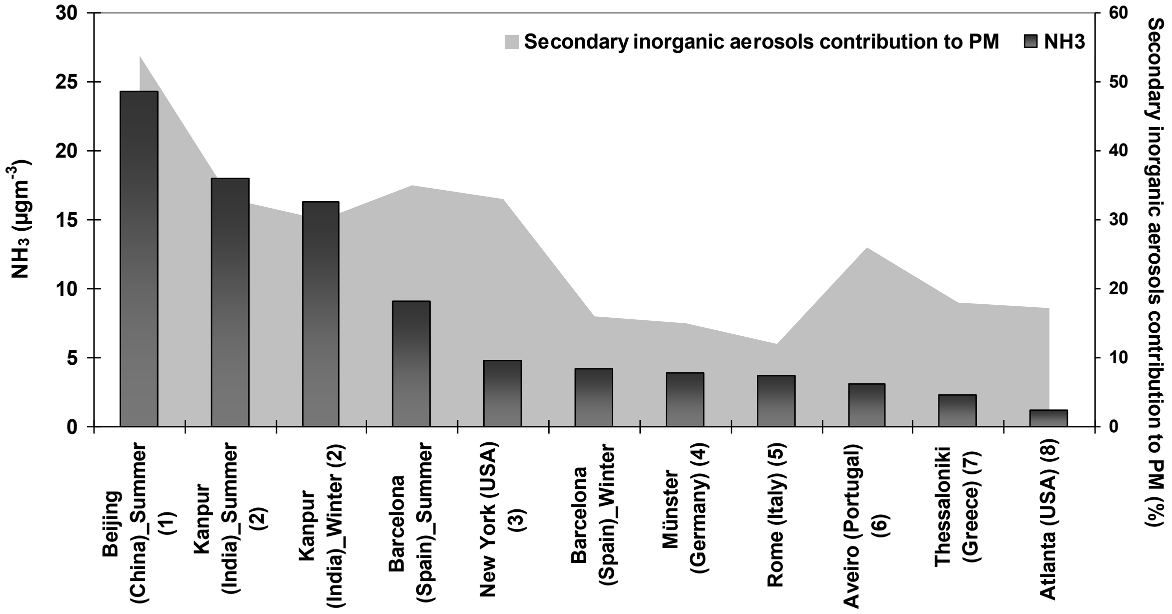

Figure 5.4. Percentage of secondary inorganic particles contribution to PM and NH_3 concentrations (µg m^{-3}) summarized in this study. The contribution of secondary particles refers to the $PM_{2.5}$ fraction except for the case of Münster and Rome which refers to the PM_{10} fraction. Numbers in brackets refer to the studies used for data compilation on secondary aerosols contribution. References about NH_3 levels are shown in Table 5.1. (1) Sun et al., 2004; (2) Behera et al., 2010; (3) Ito et al., 2004; (4) Vogt et al., 2005; (5) Perrino et al., 2010; (6) Pio et al., 2008; (7) Tsitouridou et al., 2003; (8) Modey et al., 2001.

5.2.4. Sources identification

1. Vehicular traffic

A high correlation between number of vehicle day^{-1} (Council of Barcelona, serveis de Mobilitat, 2009), and NH_3 concentrations was not obtained (r^2=0.16 in winter and r^2=0.03 in summer). However, the uncertainty of the traffic volume was high given that the traffic counts were only obtained from nearly locations and not directly next to the passive samplers. Thus, a traffic characterization campaign was designed (Figure 5.5). The two sampling points located directly on the Diagonal Avenue accounted for the highest NH_3 concentrations (6.9 and 6.5μgm^{-3}). From these traffic hot spots, NH_3 levels decreased as we moved away from the avenue. The decrease is clearly linear on the left-hand side of the avenue (in Figure 5.5), as it is a pedestrian street with no other known potential NH_3 sources affecting the measurements. The concentrations decreased down to 2.5μgm^{-3} at about 100m away from the source. This decrease was not as continuous on the right-hand side, as the street is impacted by a light but significant traffic flow (vehiclesday^{-1}) within the day. NH_3 levels decreased down to 2.9μgm^{-3} at only 50m from the main highway.

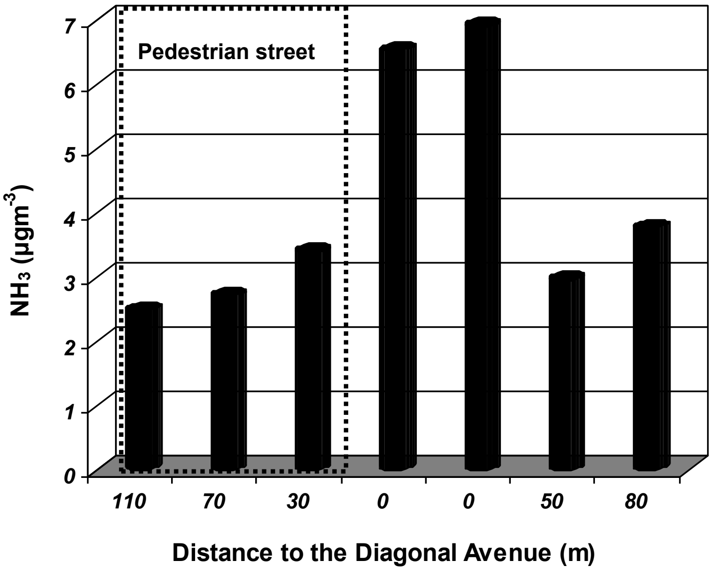

Figure 5.5. Results of the sampling campaign for the traffic impact characterization.

2. Garbage containers

Figure 5.6 shows the correlation between the number of garbage containers hm^{-2} for household and commercial wastes for seven different districts of Barcelona, according to the Statistics Department of the city council of Barcelona, and NH_3 levels per each district distinguishing the winter (r^2=0.78) and the summer (r^2=0.87) campaigns. The high positive correlation obtained indicated that garbage containers are important contributors to urban NH_3 concentrations, both in summer and in winter. In addition, a positive correlation was found between levels and the distance to garbage containers in three tests performed in the historical city centre (Figure 5.7), with levels decreasing from around 9 to 4.5 µg m^{-3} in less than 30 m. Thus, garbage containers are probably the most important controlling NH_3 source in a city with an elevated population density and where high temperature and high relative humidity are registered for long periods. The effect of the city garbage has been pointed out in previous studies (Meng et al., 2011).

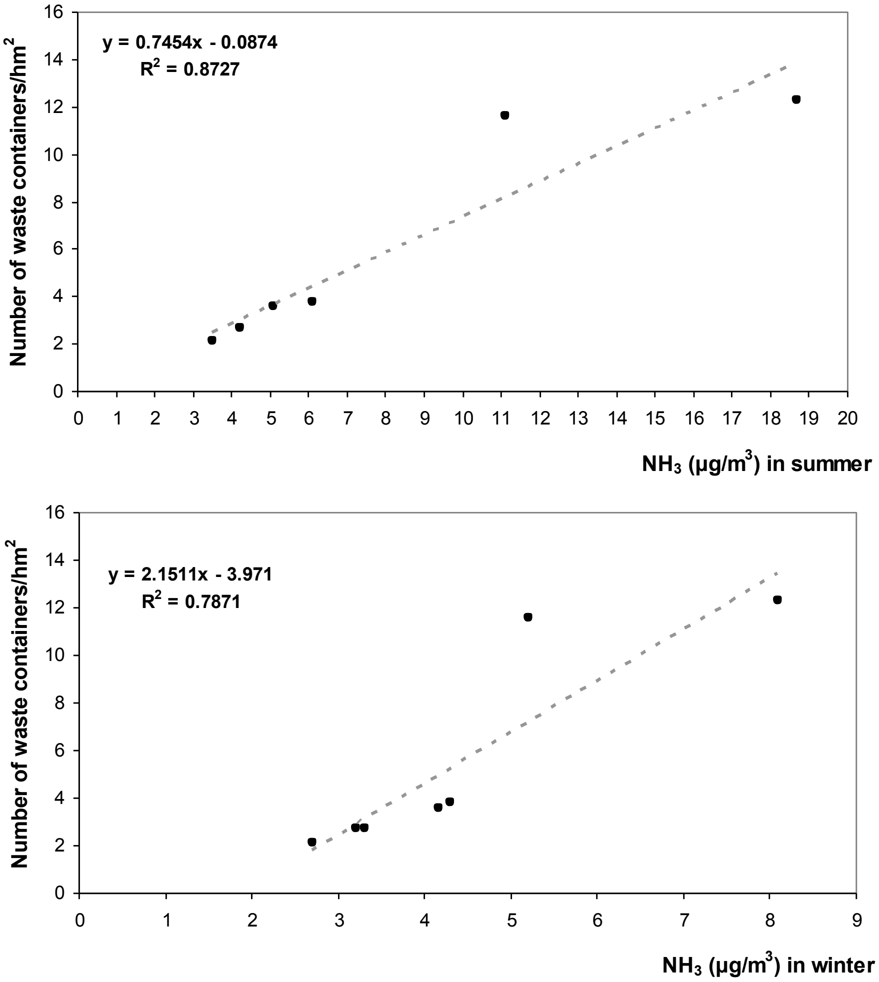

Figure 5.6. Correlations between number of waste container and NH_3 concentrations for each district of the city for the winter and the summer campaign.

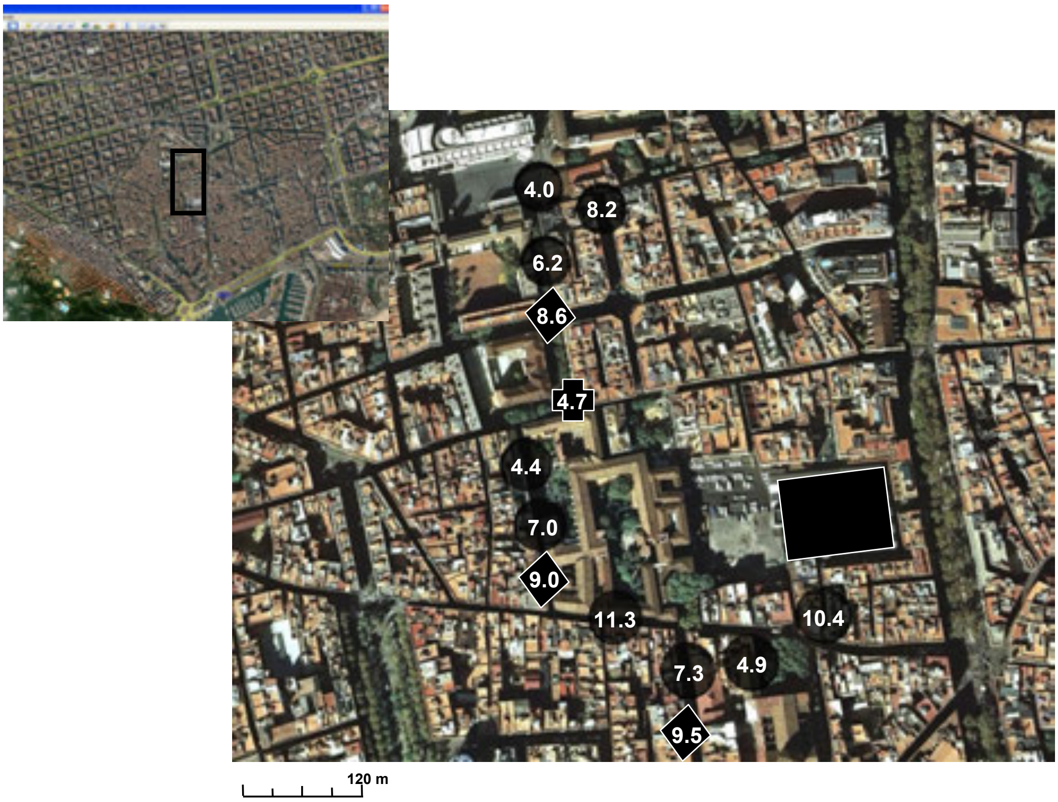

Figure 5.7. Results of the sampling campaign for sources identification in the historical city centre. ■Central open-air market; ♦Garbage container, ✚Sewer.

3. Sewage system

We attempted also to characterise the contribution of the sewage system to NH_3 levels in the city by a specific campaign following the specifications detailed in the methodology section. The average concentration for all sampling points, always measured immediately above a sewer, was 6.7 µg m^{-3}, a very similar value to those obtained near the heavy traffic sites and much higher than the average level measured at Palau Reial in the same period (2.2 µg m^{-3}). Thus, a direct impact of the sewage system emissions on local NH_3 levels seemed to have been evidenced. Differences between the sewage system emissions from the area closest to the sea and that from the uptown area were expected to be detected given its design on a slope towards the sea, finding a dependency on the height above sea level of the sampling point. However, average levels were quite similar in both areas (7.7µgm^{-3} near sea and 5.2 µg m^{-3} in the uptown area) (Table 5.3). The higher mean levels obtained near the sea were due to the selection of two points located in narrow streets in the south of the historical city centre (13.7 µg m^{-3} and 15.9 µg m^{-3}).

Table 5.3. NH_3 concentrations during the sampling campaign for the sewage system impact characterization

Sample Number	NH_3 (μgm^{-3})	Location description	
		Height above sea level (m)	Ventilaton conditions
1	6.0	21	Limited
2	13.7	6	Limited
3	15.9	6	Limited
4	3.9	4	Good
5	7.7	3	Limited
6	5.2	3	Limited
7	5.3	3	Good
8	4.1	3	Good
Mean NH_3 (μgm^{-3}) (Limited ventilation)		**9.7**	
Mean NH_3 (μgm^{-3}) (Good ventilation)		**4.5**	
9	5.1	100	Limited
10	5.1	110	Limited
11	6.9	120	Limited
12	4.7	120	Limited
13	3.9	140	Limited
Mean NH_3 (μgm^{-3})		**5.1**	

4. Open-air market

One other specific campaign aimed at characterizing the effect of garbage outside the central open market was carried out (Figure 5.7). The average level during the campaign was 7.4 µg m^{-3}. The higher levels were registered in the nearest point to the central open-air market (10.4 µg m^{-3}) and in one point in the middle of different sources but not immediately next to them (11.3 µg m^{-3}). The lowest levels were obtained in relatively open areas regardless of the distance to any source (4-4.9 µg m^{-3}). Thus, in an area characterised by narrow streets with a high population density, far above the average in Barcelona, a determining factor influencing urban NH_3 concentrations is the urban design of the streets, which in the case of the Barcelona historical city centre prevents the dispersion of air pollutants.

In sum, it can be concluded that urban NH_3 in Barcelona is strongly influenced by emissions from garbage containers. Although average NH_3 levels are high near sewers compared to those registered at an urban background site without direct impact of potential sources, the exact impact of the sewage system emission is difficult to be assess, probably because passive samplers were located high above the source (≈2m above ground to avoid vandalism). The ambient concentrations of NH_3 seem to be reduced few meters away from the immediate traffic source, except in those areas where the urban design and high human density and habits favours the accumulation of this pollutant. Overall, further research is needed.

5.2. CONCLUSIONS

The mean NH_3 levels in Barcelona during summer reached 10.6 µg m^{-3} at urban background sites (including the historical city centre) and 7.6 µg m^{-3} at traffic sites. In contrast, concentrations were higher at traffic sites (4.6 µg m^{-3}) than at urban background sites (3.9 µg m^{-3}) during winter.

The significant contribution of secondary inorganic particles detected in Barcelona compared with other cities worldwide is probably caused by the high average concentration of NH_3 measured within this study, which are in the upper range of those reported in literature, especially at the urban background sites during summer. The high relative humidity may also be responsible for this high contribution of NH_4-bearing species. This would explain the higher NO_3^- levels registered in Barcelona with respect to other Spanish cities, such as Madrid, despite the higher traffic volume.

The impact of vehicular traffic emissions on NH_3 emissions was assessed in one of the main traffic avenues in the city. A decrease in NH_3 levels of over 55% was observed as little as 50 m away from the highway, confirming the impact of vehicle emissions on this pollutant.

The study of NH_3 concentrations by districts of the city allowed us to obtain a correlation between this pollutant and the number of garbage containers per hm^2. This relation was high in summer and in winter (r^2=0.87 in summer and r^2=0.78 in winter) and shows an important impact of this source. Thus, urgent efforts are needed to better control and reduce the emissions from garbage collection systems in Barcelona, a city where the high population density together with the presence of periods of high temperatures and humidity convert wastes into a particular problem for air quality management.

The sewage system was also studied although we feel that still further research is needed for more robust conclusions to be obtained. At this stage the main observations regarding this source were: (1) average levels immediately above the source were much higher than at an urban background site with no impact of potential sources, and (2) a dependency of levels on the height above sea level was not observed.

The study of the spatial distribution of ambient NH_3 concentrations highlighted the historical city centre as the most polluted area, with levels reaching locally more than 30 µg m^{-3} in summer. The most important control on these elevated levels seems to be the emissions from garbage containers, but also the urban design of this historical area, characterised by very densely populated narrow streets, which hinders the renewal or air masses and favours the accumulation of locally derived air pollutants.

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CHAPTER 6: Carbonaceous aerosols: road traffic and biomass burning contributions to urban aerosols in a coastal mediterranean city

Parts of the results presented within this chapter have been published in Science of the Total Environment, 427-428, 175-190. Biomass burning contributions to urban aerosols in a coastal Mediterranean city.

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6. CARBONACEOUS AEROSOLS: ROAD TRAFFIC AND BIOMASS BURNING CONTRIBUTIONS TO URBAN AEROSOLS IN A COASTAL MEDITERRANEAN CITY

ABSTRACT

Mean annual biomass burning contributions to the bulk particulate matter (PM_X) load were quantified in an urban environment of Barcelona with special attention to typical Mediterranean winter and summer conditions. In spite of the complexity of the local air pollution cocktail and the expected low contribution of biomass burning emissions to PM levels in southern Europe, the impact of these emissions was detected at an urban background site by means of tracers such as levoglucosan, K^+ and organic carbon (OC). The high correlation between levoglucosan and OC (r^2= 0.77) and K^+ (r^2=0.65), as well as a marked day/night variability of the levoglucosan levels and levoglucosan/OC ratios were indicative of the contribution from regional scale biomass burning emissions during night-time transported by land breezes. In addition, on specific days (21-22 March), the contribution from long-range transported biomass burning aerosols was detected.

Quantification of the contribution of biomass burning aerosols to PM levels on an annual basis was possible by means of the Multilinear Engine (ME). Biomass burning emissions accounted for 3% of PM_{10} and $PM_{2.5}$ (annual mean), while this percentage increased up to 5% of PM_1. During the winter period, regional-scale biomass burning emissions (agricultural waste burning) were estimated to contribute with 7±4% of $PM_{2.5}$ aerosols during night-time (period when emissions were clearly detected). Long-range transported biomass burning aerosols (possibly from forest fires and/or agricultural waste burning) accounted for 5±2% of $PM_{2.5}$ during specific episodes. Annually, biomass burning emissions accounted for 19%-21% of OC levels in PM_{10}, $PM_{2.5}$ and PM_1. The contribution of this source to K^+ ranged between 48% for PM_{10} to 97% for PM_1 (annual mean). Results for K^+ from biomass burning evidenced that this tracer is mostly emitted in the fine fraction, and thus coarse K^+ could not be taken as an appropriate tracer of biomass burning.

Keywords: levoglucosan, forest fire, wildfire, open burning, agricultural residue

6.1. INTRODUCTION

Carbonaceous matter is a major constituent (up to 80%) of atmospheric aerosols in urban areas (Harrison et al., 2004; Querol et al., 2004; Yttri et al., 2009) so that understanding the sources of such material is highly relevant to particulate matter (PM) control strategies. Atmospheric emissions producing high concentrations of carbonaceous aerosols can be both anthropogenic and natural in origin.

On a global scale, models suggest that direct emission from combustion processes dominates the carbonaceous aerosol sources, amounting to 44.6 Tg yr^{-1} and 28.5 Tg yr^{-1} from tropical biomass burning and fossil fuel combustion, respectively (Gelencsér et al., 2007).

In the urban environment, traffic (especially diesel vehicles) is one of the major sources of fine carbonaceous particles, and bears the greatest responsibility for exceedings of European air quality limit values for PM (Harrison et al., 2004; Harrison and Yin, 2008; Viana et al., 2008; Pérez et al., 2010). Traffic-related air pollution is an important risk factor for respiratory morbidity and mortality. In Barcelona, the total road traffic sector emissions has been calculated in previous studies to contribute on an annual average with 46%, 51% and 48% to ambient air PM_{10}, $PM_{2.5}$ and PM_1 respectively (Amato, 2010). In addition, Pérez et al. (2010) showed that the influence of road traffic emissions on the levels of fine particulate matter was reflected in PM_1 mean annual levels, which show a significant increasing trend, and a good correlation with the progressive rise in road traffic flow and the growth of the diesel fleet in Barcelona.

Another important anthropogenic contributor to the carbonaceous aerosol burden in many urban environments is biomass burning for residential heating purposes, notably by wood burning stoves (Ward et al., 2006; Szidat et al., 2007; Alfarra et al., 2007; Sandradewi et al., 2008a). Additional polluting intrusions of biomass burning aerosols derive from forest fires (Yttri et al., 2005; Saarikoski et al., 2008) and burning of agricultural wastes (Zhang et al., 2007; Lee et al., 2008a).

Biomass combustion emissions contribute with significant amounts of particulate matter (PM), inorganic species, and thousands of organic compounds to ambient air (Radzi et al., 2004). Domestic wood burning may be the main contributor to air quality degradation in rural areas in wintertime (Ward et al., 2006; Szidat et al., 2007; Alfarra et al., 2007; Sandradewi et al., 2008b). Therefore, biomass combustion both controlled and from wildfires, has become an important issue in air pollution as a primary source of particles both in urban and rural areas (Charlson et al., 1992; Fang et al., 1999; Simoneit, 2001).

The quantity and composition of the numerous organic compounds released from biomass burning depend on various factors, such as the fuel composition, burn rate, the topography and morphology of the terrain and the weather conditions (Gullett et al., 2003; Fine et al., 2004; Jordan and Seen, 2005; Hedberg et al., 2006; Saarikoski et al., 2008). Because of the chemical complexity of biomass burning emissions, suitable tracers for this emission source are not easily found. Although water soluble potassium has been suggested as a tracer for wood smoke in receptor models (Echalar et al., 1995; Khalil and Rasmussen, 2003), it is also emitted by other sources in urban areas such as meat cooking and refuses incineration (Olmez et al., 1988; Sheffield et al., 1994; Schauer et al., 1999). In contrast, biopolymer degradation products such as levoglucosan (1.6-anhydro-β-D-glucopyranose) from cellulose, hemicellulose or lignite (Fabbri et al., 2009) have been proposed as tracers for biomass burning since, to date at least, no other sources are known to exist (Simoneit et al., 1999). Levoglucosan is accompanied in atmospheric aerosols by other stereoisomeric monosaccharide anhydrides, mannosan (1, 6-anhydro-β-D-mannopyranose) and galactosan (1,6-anhydro-β-D-galactopyranose) that result from the pyrolysis of hemicellulose. Emitted amounts of mannosan and galactosan are substantially lower than those of levoglucosan (Zdráhal et al., 2002). Levoglucosan is emitted in concentrations large enough to be easily analysed and it is mostly associated with fine aerosols (Fraser and Lakshmanan, 2000). Previous papers have reported that levoglucosan can show a maximum preference for the 0.34-0.56 μm size mode (Yttri et al., 2005; Saarikoski et al., 2008), suggesting that wood smoke aerosols increase in size as they age in the environment and that considerable mass in the <0.2 μm size mode means a fresh, local source (Cahill, 2010). Thus the contribution of biomass burning emissions to air quality is hard to determine due to the fact that although there are several potential chemical tracers, there is no single specific tracer to easily identify and calculate the contribution of the source.

Levoglucosan has been studied not only in wood burning emission samples but also in the ambient air, with many studies having now detected its presence due to biomass combustion processes in rural, suburban and urban air samples in North and South America, Africa, Europe and China (see Table 6.2 for values and references). Such studies have shown that whereas in the American Continent and North Europe major biomass burning emissions are mostly linked to wood smoke from fireplaces and stoves (Freeman and Cattell, 1990; Zheng et al., 2002; Puxbaum et al., 2007 and references in Table 6.2), in southern European countries wildfires and agricultural wastes burning can be the most important biomass combustion sources (Oliveira et al., 2007; Pio et al., 2008), especially in summer. The impact of wildfire episodes was studied in summer 2007 and 2009 in Greece and Portugal, respectively; both studies reported a significant input of wildfires to the atmospheric levels at regional and local scales (Alves et al., 2011; Kaskaoutis et al., 2011).

Source apportionment studies indicate relatively high contributions of the biomass burning source in winter in Central and Northern European areas (Switzerland, Szidat et al., 2006, 2007; Lanz et al., 2010), and also during the CARBOSOL project (Puxbaum et al., 2007). Estimates of the contribution of domestic heating to $PM_{2.5}$ emissions vary from city to city (Denby et al., 2010). Previous studies account for a contribution of up to 80% from wood combustion in Oslo (Larssen et al., 2006) while in Denmark wood burning represented around 47% of all Danish $PM_{2.5}$ emissions (Palmgren et al., 2005). Cities such as Helsinki have less significant contributions with wood burning estimated to account for just 24% of the local emissions (Kauhaniemi et al., 2008). However, in smaller cities in Finland and Denmark wood burning is estimated to be the dominating emission source. This percentage is expected to be much lower in south European cities where wood burning residential installations are infrequent (in Spain the number is estimated in less than 2000 installations in the entire country; www.avebiom.org) and mostly located in rural and suburban areas. However, to the authors' knowledge no detailed estimations are currently available for Mediterranean regions.

The aim of the work presented here is to study the mean annual contribution of carbonaceous aerosol sources using a receptor modelling approach (Multilinear Engine, ME-2). Given the limited information of biomass burning impact in Spain, we found interesting to deeply investigate the concentrations in ambient air of biomass combustion tracers, such as levoglucosan, in the urban environment of Barcelona. Our goal is firstly to check if concentrations are high enough to be detected, then to compare them with values obtained in urban environments in other geographical areas where biomass combustion has generally a major influence.

To the purpose of this work, data collected in the urban background station of Torre Girona during 2009 was analysed, including the DAURE campaign, which, as previously described in the methodology section, provided additional information regarding on-line and off-line measurements. In brief, we will discuss data from (a) chemical analysis of major and minor inorganic compounds, including soluble major tracers compounds from PM_{10}, $PM_{2.5}$ and PM_1 samples, and of molecular ions of monosaccharide anhydrides (levoglucosan, mannosan and galactosan), and (b) on-line measurement from a multi-angle absorption photometer (MAAP), two PM optical counters (Grimm Labortechnik GmbH & Co. KG; models 1107 and 1108), an Aerodyne high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS), real time monitors for gaseous pollutants: NO, NO_2 (SIR S-5012), CO (Ecothec EC 9830), O_3 (SIR S-5014) and SO_2 (Thermo Scientific Model 43C) and a proton transfer reaction-mass spectrometer (PTR-MS from Ionicon Analytik Innsbruck, Austria). Additionally, 120 h back-trajectories ending in Barcelona were calculated with the Hysplit model.

6.2. RESULTS AND DISCUSSION

6.2.1. Comparison with other European cities

Table 6.1 summarizes the levels of EC, OC and OC/EC reported in previous works for different backgrounds in European cities covering different climatic regions. The ratios OC/EC in Barcelona for the PM_{10} and the $PM_{2.5}$ fraction are in the same range as those reported at other urban background sites in cities with a high density of vehicles and slightly higher than at kerbsites. Maximum ratios are obtained for rural or continental sampling stations and, for most of them, values are especially elevated in summer, as shown for those sites where the information was available separately for the winter and summer period. This fact is probably related with an enhancement of secondary formation processes mediated by photochemistry in clean atmospheres in summer when higher temperatures and higher solar radiation.

Table 6.1. Concentrations of Organic (OC; μgm^{-3}) and Elemental Carbon (EC; μgm^{-3}) and OC/EC reported for different backgrounds in European cities.

City	Background	EC	OC	OC/EC		Size fraction	Methodology	Study
Athens (Greece)	Urban	1.8±0.6	5.7±2.8	3.2	0.316	<10	TOT[1]	Prosmitis et al., 2003
Rome (Italy)	Urban	3.75±0.2	4.77±0.6	1.3	0.786	<10	TOT[1]	Avino et al., 2004
Athens (Greece)	Urban	2.72±1.7	6.64±2.5	2.4	0.410	unspecified	TOT[1]	Prosmitis et al., 2004
	Urban-traffic	6.7±2.8	9.9±0.8	1.5	0.677			
Vienna (Austria)	Urban	3.3	4.0	1.2	0.825	<2.5	TOT[1]	Puxbaum et al., 2004
Santa Cruz de Tererife (Spain)	Urban	1.5±0.1	2.6±0.2	1.7	0.577	<2.5	TOT[1]	Alastuey et al., 2004
Bern (Switzerland)	Urban-traffic	4.2	5.4	1.3	0.778	<2.5	TOT[1]	Hueglin et al., 2005
		5.6	6.4	1.1	0.875	<10		
Zurich (Switzerland)	Urban	2	3.5	1.8	0.571	<10	TOT[1]	Hueglin et al., 2005
		1.8	3.4	1.9	0.529	<2.5		
Oslo (Norway)	Urban	4.6	7.6	1.7	0.605	<10	TOT[1]	Yttri et al., 2005
		2.2	3.9	1.8	0.564	<2.5		
Amsterdam (Holland)_winter	Urban	1.7±0.9	6.7±3.8	3.9	0.254	<2.5	TOT[1]	Viana et al., 2007
Amsterdam (Holland)_summer		1.9±0.7	3.9±1.6	2.1	0.487			
Barcelona (Spain)_winter	Urban	2.6±1.4	6.9±2.5	2.7	0.377	<2.5	TOT[1]	Viana et al., 2007
Barcelona (Spain)_summer		1.5±0.7	3.6±1.4	2.4	0.417			
Ghent (Belgium)_winter	Urban	1.2±0.6	5.4±4.5	3.8	0.267	<2.5	TOT[1]	Viana et al., 2007
Ghent (Belgium)_summer		0.8±0.3	2.7±1.0	3.4	0.296			
Aveiro (Portugal)_winter	Rural	1.8	12.3	6.8	0.146	<2.5	TOT[1]	Gelencsér et al., 2007
Aveiro (Portugal)_summer	Rural	0.57	3.47	6.1	0.164			
Puy de Dôme (France)_winter	Continental	0.21	0.62	3.0	0.339	<2.5	TOT[1]	Gelencsér et al., 2007
Puy de Dôme (France)_summer	Continental	0.29	4.63	16.0	0.063			
Schauinsland (Germany)_winter	Rural	0.28	1.38	4.9	0.203	<2.5	TOT[1]	Gelencsér et al., 2007
Schauinsland (Germany)_summer	Rural	0.12	1.44	12.0	0.083			
Sonnblick (Austria)_winter	Continental	0.02	0.19	9.5	0.105	<2.5	TOT[1]	Gelencsér et al., 2007
Sonnblick (Austria)_summer	Continental	0.12	1.44	12.0	0.083			
K-Puszta (Hungary)_winter	Rural	1.74	8.91	5.1	0.195	<2.5	TOT[1]	Gelencsér et al., 2007
K-Puszta (Hungary)_summer	Rural	0.53	4.52	8.5	0.117			
Oporto (Portugal)	Urban	1.4	1.5	1.1	0.933	<0.49	TOT[1]	Duarte et al., 2008
		0.6	1.9	3.2	0.316	0.49-0.95		
		0.35	1.3	3.7	0.269	0.95-3.00		
		0.2	1.2	6.0	0.167	3.00-10.00		
Toulouse (France)	Urban	1.95±1.06	4.71±1.61	2.4	0.414	<2.5	TOT[1]	Calvo et al., 2008
		2.05±1.11	5.02±1.60	2.4	0.408	<10		
London (UK)	Urban-traffic	8.2±1.0	7.1±0.8	0.9	1.155	<10	TOT[1]	Kulbusch et al., 2009
Huelva (Spain)	Urban	1.5	3.5	2.3	0.429	<10	TOT[1]	Sánchez de la Campa et al., 2009
		1.1	2.9	2.6	0.379	<2.5		
Prague (Czech. Republic)	Urban-traffic	1.53±0.3	1.90±0.3	1.2	0.805	<2.5	TOT[1]	Ondráček et al., 2011
Madrid (Spain)	Suburban	1.34±1.3	3.74±0.9	2.8	0.358	<2.5	ACPM[2]	Plaza et al., 2011
Barcelona (Spain)	Urban	1.53	3.07	2.0	0.498	<10	TOT[1]	This study
		1.33	2.62	2.0	0.508	<2.5		
		1.12	2.18	1.9	0.514	<1		

[1] Thermal-optical transmission technique.

[2] Ambient Carbonaceous Particle Monitor-ACPM, Rupprecht and Patashnick model 5400, Thermo Scientific Inc.).

It is important to note that differences in ratios between north European (e.g. Vienna, Zurich or Oslo) and south European cities (e.g. Rome, Athens, Huelva or Barcelona) at urban background sites are negligible and it is not easy to conclude a different contribution of secondary organic carbon depending on climatic factors or sources. In addition, the range of values of OC/EC ratios for biomass burning emissions in literature is too large to allow concluding which regions are mainly affected by this source (Fine et al., 2004; Sullivan et al., 2008 and Saarnio et al., 2010b).

The significant impact of traffic in the city of Barcelona has been reported in previous studies (e.g. Pérez et al., 2010; Amato et al., 2011). In chapter 4, we saw the high density of vehicles in the city compared to other European megacities, as well as elevated levels of BC clearly governed by this source. Amato et al. (2011) showed simultaneous data from one urban background (TG), one traffic, and one heavy traffic location in the city and calculated roadside PM_{10} enrichments in a number of elements arising from vehicular emissions. Tracers of primary traffic emissions (EC, Fe, Ba, Cu, Sb, Cr, Sn) showed the largest enrichment (>70%). Other traffic tracers (Zr, Cd) showed lower but still consistent enrichments (25–40%), similar to those obtained for mineral matter resulting from road dust resuspension (Ca, La, Ce, Ti, Ga, Sr, 30–40%). The sum of primary and secondary organic carbon were 41% higher near traffic, with contributions of secondary OC (SOC) to total OC ranging from 46% at the heavy traffic site, 63% at the traffic site and 78% in TG. At this point of knowledge about the influence of traffic in the city of Barcelona and its contribution to primary and secondary aerosols, it was importat to also analyse the impact of biomass burning emissions to widely understand the carbonaceous aerosol origin, as biomass burning has been described as a major source in many northern European cities, especially during the cold season. To that end, in this study the monosaccharide anhydrides (MA) levoglucosan, mannosan and galactosan were determined from the $PM_{2.5}$ fraction collected on quartz filters as tracers of biomass burning emissions. The selection of size ranges other than $PM_{2.5}$ is not likely to affect substantially the results, since about 80 percent of the MA is in the particles smaller than 1µm (Yttri et al., 2005; Saarikoski et al., 2008).

It is worthwhile to note that three additional sets of levoglucosan concentrations are available for the DAURE campaign from different PM fractions and different length of sampling periods obtained by different laboratories. The description of methodologies and comparisons among sets are shown in Minguillón et al. (2011). These authors found a high correlation between data sets. The data set analysed in the present work was provided by the Finnish Meteorological Institute, as it covers the whole campaign and with a higher temporal resolution.

Correlations between the three isomers (levoglucosan, mannosan and galactosan) are shown in Figure 6.1. The lack of relationship for some days is probably related to the uncertainty in the determination of very low concentrations of mannosan or galactosan in the samples. Differences between levoglucosan and mannosan or galactosan can also result from a variance in cellulose and hemicellulose content in burned biomass materials (Zdráhal et al., 2002).

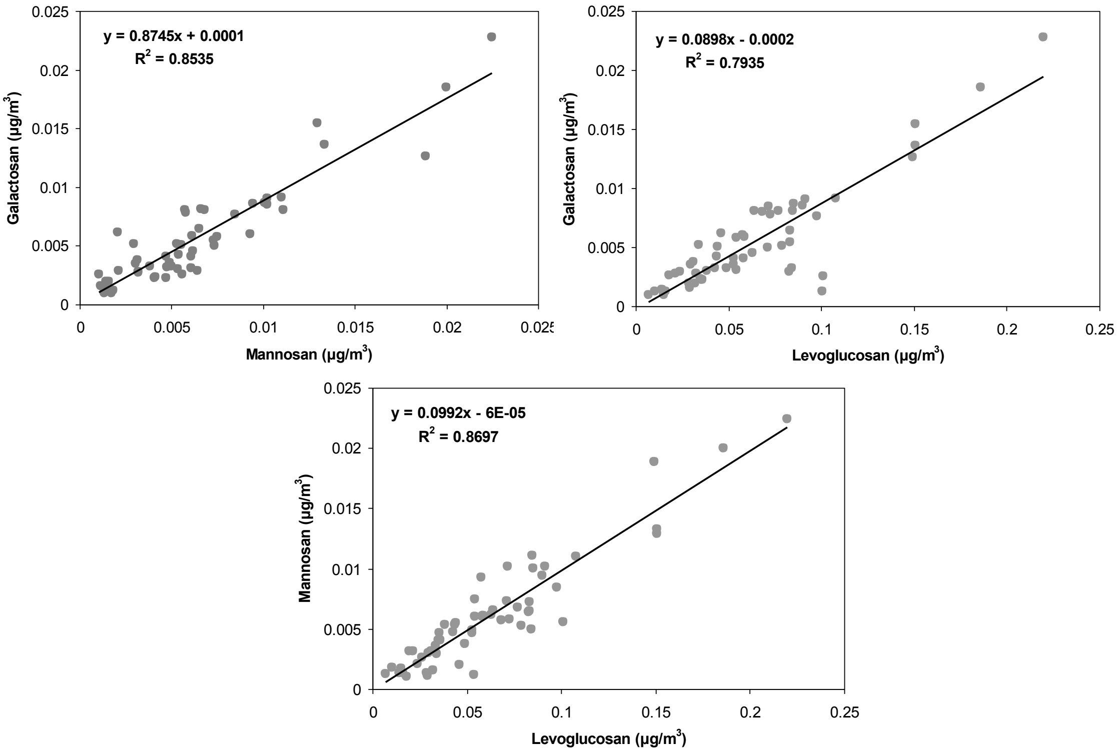

Figure 6.1. Correlations between biomass burning tracers (levoglucosan, mannosan and galactosan).

As expected, levoglucosan was the most abundant isomer accounting for up to 80% of the sum of the three isomers analysed, which is within the range of previous studies (Zdráhal et al., 2002), followed by mannosan (11%) and galactosan (9%). Levoglucosan contributions have been widely described for urban, rural and continental sites in Northern and Central European regions, whereas much less information is available for southern Europe (Oliveira et al., 2007; Pio et al., 2008). Levels in winter in Barcelona (north-eastern Spain, Table 6.2) were 0.06 µg m^{-3} on average, in the range of those obtained in urban sites in winter in Copenhagen (0.04 µg m^{-3}; Oliveira et al., 2007) and Gothenburg (0.06 µg m^{-3}; Szidat et al., 2009). However, results reported in these cities are unusually low when compared with other urban and suburban sites in Scandinavia during wintertime sampling, such as Lycksele (0.9 µg m^{-3}; Hedberg et al., 2006) and Oslo (0.17 µg m^{-3}; Yttri et al., 2005), and it would seem that these values cannot be taken as representative of these Northern latitudes. In the case of Gothenburg, authors attributed the low concentrations found to the state of the combustion technology, the nature of the appliances used and the extended use of distinct heating, as the production of levoglucosan is reduced for higher combustion temperatures (Schmidl et al., 2008), as well as to the clean air masses from marine or low-populated land areas entering the city. Likewise, in the Copenhagen study it is stated that the city is characterized by a heating system from power stations with very efficient emissions control (Oliveira et al., 2007). In central European cities, significantly higher levoglucosan levels have been measured in winter (Table 6.2), e.g. Zurich (0.62 µg m^{-3}, Szidat et al., 2006), Ghent (0.42-0.48 µg m^{-3}, Zdrahal et al., 2002; Paschynska et al., 2002) or Graz (0.82 µg m^{-3}, Caseiro et al., 2009). Regarding the southern European regions, Oliveira et al. (2007) reported an average concentration of levoglucosan of 0.12µgm^{-3} during wintertime in an urban site in Oporto (Portugal), while Sillanpää et al. (2005) showed very low levels of MA in Barcelona (0.06 µg m^{-3}) and Athens (0.045 µg m^{-3}) for the spring and summertime, respectively. Both studies described a minor impact of biomass burning in these regions, although the selected sampling period in Sillanpää et al. (2005) did not allow concluding a lower use of wood burning for heating or cooking, but a negligible influence from frequent wildfires taking place during the warm seasons in forested areas.

Such differences between European countries consequently indicate that different national policies and control strategies might be needed to achieve a reduction of carbonaceous aerosol levels on a continental scale, if biomass burning emissions were targeted.

Table 6.2. Concentrations of levoglucosan (µgm^{-3}) and monosaccharide anhydrides (ΣMA, means sum of levoglucosan, mannosan and galactosan) reported for different backgrounds (adapted from Szidat et al., 2009).

Study	Site	Background	Date	Size	Levoglucosan (µg/m^3)	ΣMA
Fraser and Lakshmanan et al., 2000	Dallas (USA)	Urban	May (1998)	PM_{10}	0.5	-
Zdrahal et al., 2002	Ghent (Belgium)	Urban	Jan-Mar (1998)	PM_{10}	0.48	0.56
Pashynska et al., 2002	Ghent (Belgium)	Urban	Nov-Mar (2000/01)	PM_{10}	0.42	0.51
Yttri et al., 2005	Oslo (Norway)	Urban	Nov-Dec (2001)	PM_{10}	0.17±0.15	0.21±0.19
	Elverum (Norway)	Urban	Jan-Mar (2002)	PM_{10}	0.41±0.22	0.53±0.28
Sillanpää et al., 2005	Amsterdam (NL)	Urban	Jan-Mar (2003)	$PM_{2.5}$	-	0.36±0.25
	Athens (Greece)	Urban	June-July (2003)	$PM_{2.5}$	-	0.045±0.005
	Barcelona (Spain)	Urban	Mar-May (2003)	$PM_{2.5}$	-	0.06±0.03
Hedberg et al., 2006	Lycksele (Sweden)	Urban	Jan-Mar (2002)	PM_{10}	0.9	-
Leithead et al., 2006	Fraser Valley (Canada)	Urban	Aug (2001)	$PM_{2.5}$	0.014	-
Szidat et al., 2006	Zurich (Switzerland)	Urban	Feb (2003)	PM_{10}	0.62±0.16	-
Puxbaum et al., 2007	Azores (Portugal)	Maritime	Dec-Feb (2002/03) Dec-Feb (2003/04)	$PM_{2.5}$	0.006	-
	Aveiro (Portugal)	Rural	Dec-Feb (2002/03) Dec-Feb (2003/04)	$PM_{2.5}$	1.2	-
	Puy de Dôme (France)	Continental	Dec-Feb (2002/03) Dec-Feb (2003/04)	$PM_{2.5}$	0.02	-
	Schauinsland (Germany)	Rural	Dec-Feb (2002/03) Dec-Feb (2003/04)	$PM_{2.5}$	0.03	-
	Sonnblick (Austria)	Continental	Dec-Feb (2002/03) Dec-Feb (2003/04)	$PM_{2.5}$	0.013	-
	K-Puszta (Hungary)	Rural	Dec-Feb (2002/03) Dec-Feb (2003/04)	$PM_{2.5}$	0.6	-
Oliveira et al., 2007	Oporto (Portugal)	Urban	Nov-Dec (2003)	PM_{10}	0.12±0.08	-
	Copenhagen (DK)	Urban	Feb-Mar (2004)	$PM_{2.5}$	0.04±0.04	-
Wan & Yu, 2007	Hong Kong (China)	Urban	Aug (2004)-April (2005)	PM2.5	0.19	-
Glasius et al., 2008	Vindinge (Denmark)	Urban	Feb-April (2005)	$PM_{2.5}$	0.17±0.09	-
Pio et al., 2008	Aveiro (Portugal)	Rural	Aug-Sept (2003)	$PM_{2.5}$	0.058	-
Saarikoski et al., 2008	Duisburg (Germany)	Urban	Oct-Nov (2002)	$PM_{2.5}$	-	0.23±0.13
	Helsinki (Finland)	Urban	Mar-May (2002)	$PM_{2.5}$	-	0.08±0.07
	Prague (CZ)	Urban	Nov-Jan (2002/03)	$PM_{2.5}$	-	1.32±0.50
Sandradewi et al., 2008	Zurich (Switzerland)	Urban	Jan (2006)	PM_{1}	0.31±0.16	0.41±0.21
Szidat et al., 2009	Gothenburg (Sweden)	Urban	Feb-Mar (2005)	$PM_{2.5}$	0.06±0.03	0.09±0.05
	Råö (Sweden)	Rural	Feb-Mar (2005)	PM_{10}	0.04±0.02	-
Caseiro et al., 2009	Vienna (Austria)	Urban	Jan-Feb, Dec (2004)	PM_{10}	0.24	-
	Graz (Austria)	Urban	Jan-Feb, Dec (2004)	PM_{10}	0.82	-
	Salzburg (Austria)	Urban	Jan-Feb, Dec (2004)	PM_{10}	0.31	-
Saarnio et al., 2010b	Helsinki (Finland)	Urban	August (2006)	PM_{1}	0.15	-
Bari et al., 2010	Dettenhausen (Germany)	Regional	Nov (2005)- March (2006)	PM_{10}	0.806	-
Křůmal et al., 2010	Šlapanice (Czech Republic)	Urban	Feb (2009)	PM_{1}	0.42	-
	Šlapanice (Czech Republic)	Urban	Feb (2009)	$PM_{2.5}$	0.57	-
	Brno (Czech Republic)	Urban	Feb (2009)	PM_{1}	0.22	-
	Brno (Czech Republic)	Urban	Feb (2009)	$PM_{2.5}$	0.32	-
This study	Barcelona (Spain)	Urban	Feb-Mar (2009)	$PM_{2.5}$	0.06	0.07

6.2.2. Variability of biomass burning tracers

A significant day-night variability of levoglucosan levels was detected (mean ratio night/day=1.5). This variability could be due to two processes: (a) the concentration of pollutants in the lower nocturnal boundary layer height, and/or (b) the transport towards Barcelona of biomass burning emissions generated on the regional-scale by means of the night-time land breeze. A third option, the higher biomass burning emissions during the night (possibly due to residential heating), is possible but less likely than the previous processes, due to the mean temperatures recorded during the DAURE campaign (12-15ºC). Thus, only night-time levels are shown in order to better interpret episodes of this source.

Figure 6.2 shows the time series of levoglucosan and K^+ in Barcelona during night. Two marked peaks of biomass burning tracers can be observed on 27th February and 13th March of 2009, both occurring during the polluted scenarios (B) described in Pandolfi et al. (2012a), with marked atmospheric inversions causing important accumulation of urban aerosols. Thus, these two maxima cannot be linked to days with increased biomass burning emissions, but rather to atmospheric conditions preventing dilution of pollutants. Maximum daily levels of levoglucosan, galactosan and mannosan reached 0.2, 0.02 and 0.02μgm^{-3}, respectively. Time series of $PM_{2.5}$, BC and OC (Figure 6.2b) showed a similar variability as biomass burning tracers, with levels dropping to minima during Atlantic advection episodes and attaining maxima during local anticyclonic conditions. This confirms the influence of meteorology on levoglucosan levels (as well as other pollutants). Indeed, levoglucosan represents a rather constant percentage of the total $PM_{2.5}$ mass of 0.3% during both sorts of pollution conditions.

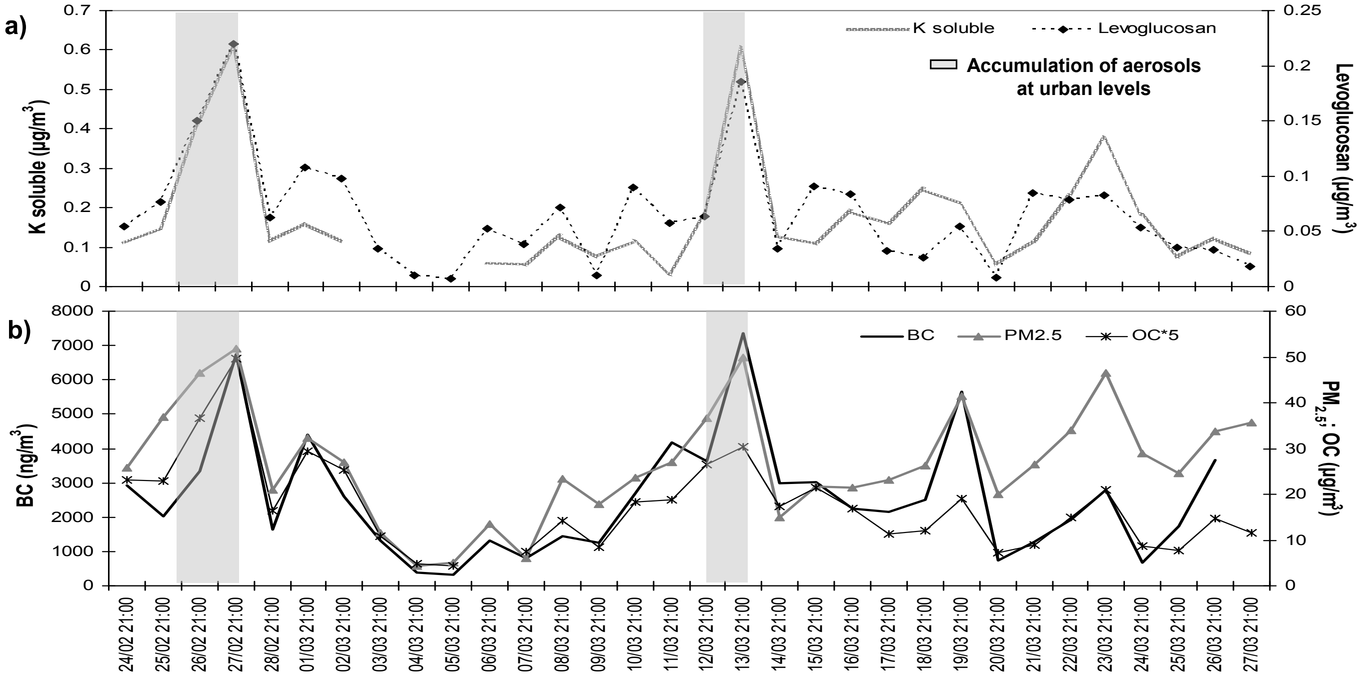

Figure 6.2. Time series of the atmospheric pollutants concentrations for the night period of: a) Levoglucosan and K^+ and b) BC, $PM_{2.5}$ and OC. Days with accumulation of pollutant at urban levels are highlighted in grey.

In order to identify days with potential biomass burning episodes, time series of levoglucosan/OC, levoglucosan/$PM_{2.5}$, K^+/OC and K^+/$PM_{2.5}$ for the whole campaign were analysed. In agreement with the reported influence of other sources on K^+ levels (Zhang et al., 2010; Aiken et al., 2010), no relevant information could be extracted from the analysis of time series of K^+/OC and K^+/$PM_{2.5}$ (not shown in this work). Differences in levoglucosan/OC and levoglucosan/$PM_{2.5}$ ratios were observed for day and night periods (Figure 6.3), suggesting different emission sources of these compounds during day and night (e.g. higher ratios occurring at night were probably due to the land breeze transport of regional biomass burning emissions towards Barcelona and/or to lower emissions from other urban sources, such as road traffic) or less stability of levoglucosan during day due to higher temperatures and/or oxidation by free radicals (OH) under high relative humidity conditions (Hennigan et al., 2010; Hoffmann et al., 2010). The latter option is less probable due to the reported stability of this compound in winter (Mochida et al., 2010) and the negligible differences between day and night temperature (3ºC lower at night) and relative humidity (8% higher at night) during the sampling period. Thus, maxima at nights suggest the presence of emissions of biomass burning tracers which originated on the regional scale, possibly derived from open burning of agricultural residues (biomass burning emissions inside the city are not expected to be significant as only 0.2% of residences use biomass burning for heating while 65% use natural gas and 30% electricity, according to data from the city council of Barcelona). The presence of woodburning is confirmed by levoglucosan mass concentrations, which are about 10-70% higher at night than during the day for 65% of the sampling days (as opposed to $PM_{2.5}$ or OC similar or lower during night, see Table 6.3). In addition, it is worthwhile to draw attention to days 21st-22nd March (outside of the accumulation events), when levoglucosan/OC ratios were at their highest and differences between day and night were not observed (ratios of 0.041 and 0.038 on average for day and night periods, respectively). The time series of levoglucosan levels shows the same lack of day and night variation from 21st-23th March, confirming that the behaviour of the ratio is showing a remarkable episode, but indicating also that it is not possible to accurately narrow the length of that episode with the available time resolution. This episode was interpreted as days under the influence of air masses loaded with long-range transported pollutants, increasing levoglucosan levels, and potentially originating from sources such as forest fires and or agricultural fires, among others. During 21st-22nd March, the analysis of 120h backtrajectories performed with the Hysplit model evidenced that air masses had a European origin (Figure 6.4), although these days may have been characterized by intense anticyclonic conditions on the surface levels. However, the hysplit model resolution does not allow confirming this local air mass circulation. For these days the MODIS Rapid Response System, which provides daily satellite images of the Earth's landmasses in near real time, detected a significant number of fires in north-eastern Spain and south-western France (Figure 6.4).

The levogucosan/OC ratio was 0.045±0.010 during the days with potential influence of forest fires or agricultural waste burning. It is in the range of those reported for softwood combustion in previous studies (Fine et al., 2002; Sullivan et al., 2008). This ratio was 0.015±0.010 for days when regional-scale biomass burning emissions were detected at the sampling point by means of the day and night variations of levoglucosan levels discussed above.

The levoglucosan-to-mannosan (L/M) and the levoglucosan-to-mannosan plus galactosan (L/(M+G)) ratios have been used to distinguish different biomass burning sources in several studies (Fine et al., 2004; Ward et al., 2006; Engling et al., 2006;

Schmidl et al., 2008; Caseiro et al., 2009; Fabbri et al., 2009). The average L/M and L/M+G ratios during days 21th-22nd are 5.6 and 5.0, respectively. These values are in the order of those reported in Ward et al. (2006) for forest fire smoke and particularly for softwood fires (Fine et al., 2004).

Conversely, on days under the influence of regional-scale biomass burning contribution, the L/M ratio ranged between 5- 44 and the ratio L/M+G was between 3 and 10. This large variability is in accordance with the wide range of values reported in the literature for atmospheric aerosol samples. These values were compiled by Fabbri et al. (2009), accounting for a range of 3-75 and 3-14 for L/M and L/M+G ratios, respectively. These authors found L/M and L/M+G ratios larger than 30 for lignite combustion, but recommended that due to possible mixing of smoke from burning of lignite and biomass, and due to the high values of the L/M and L/M+G ratios for some hardwoods and grasses, caution should be used when interpreting sources of anhydrosaccharides in environmental samples.

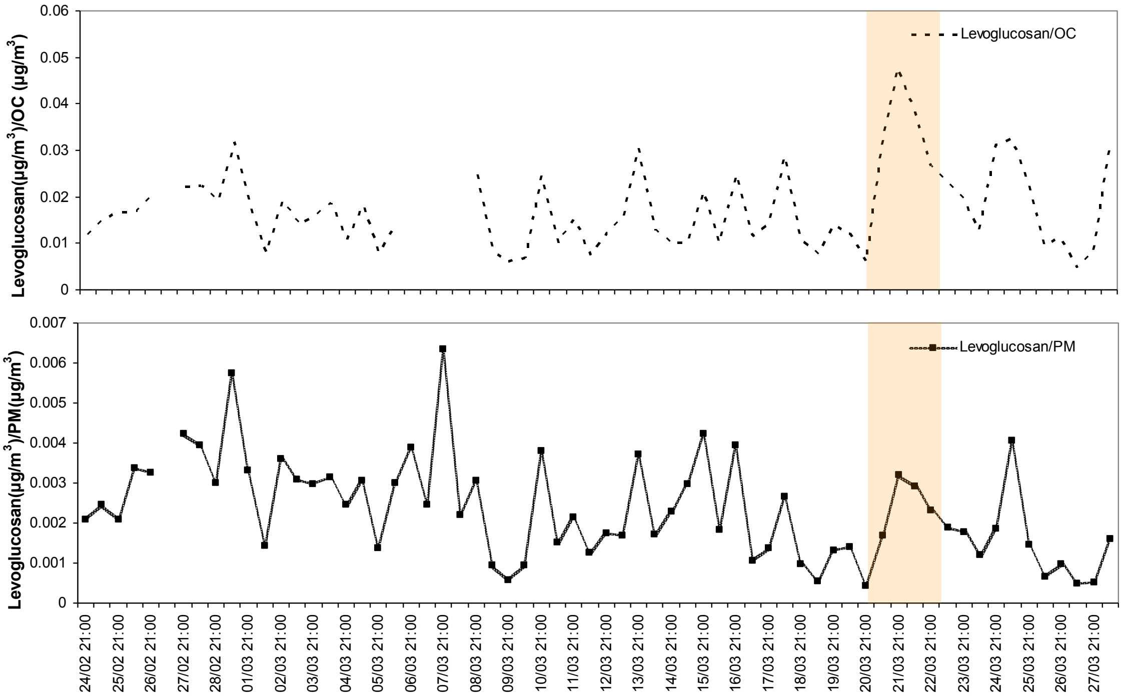

Figure 6.3. Ratios of levoglucosan/OC and levoglucosan/PM$_{2.5}$ for the whole campaign. Days with a potential influence of forest fires at the studied site are indicated in orange.

Table 6.3. Average concentrations and standard deviation of major atmospheric pollutants for the DAURE sampling period.

	Average concentrations					
	Total		Day		Night	
	Average	St. Deviation	Average	St. Deviation	Average	St. Deviation
$PM_{2.5}$ (μg/m^3)	26.9	11.6	27.1	11.0	26.8	12.4
OC (μg/m^3)_$PM_{2.5}$	3.6	1.9	3.6	1.8	3.5	2.0
EC (μg/m^3)_$PM_{2.5}$	1.5	0.9	1.4	0.7	1.7	1.1
Levoglucosan (μg/m^3)_$PM_{2.5}$	0.06	0.04	0.05	0.04	0.07	0.04
Mannosan (μg/m^3)_$PM_{2.5}$	0.006	0.004	0.005	0.004	0.007	0.005
Galactosan (μg/m^3)_$PM_{2.5}$	0.005	0.004	0.004	0.003	0.006	0.005
K (μg/m^3)_$PM_{2.5}$	0.19	0.10	0.19	0.09	0.19	0.11
K^+ (μg/m^3)_$PM_{2.5}$	0.17	0.13	0.17	0.1	0.18	0.14
BC (μg/m^3)_PM_{10}	2.5	1.4	2.3	1.2	2.6	1.7
NOx (μg/m^3)	58.1	36.6	50.2	26.4	66	43.5
CO (μg/m^3)	0.64	0.20	0.64	0.18	0.63	0.27
Acetonitrile (ppbv)	0.30	0.20	0.28	0.14	0.33	0.26
***m/z* 60 (ToF-AMS)_PM_1**	0.033	0.020	0.032	0.025	0.034	0.020

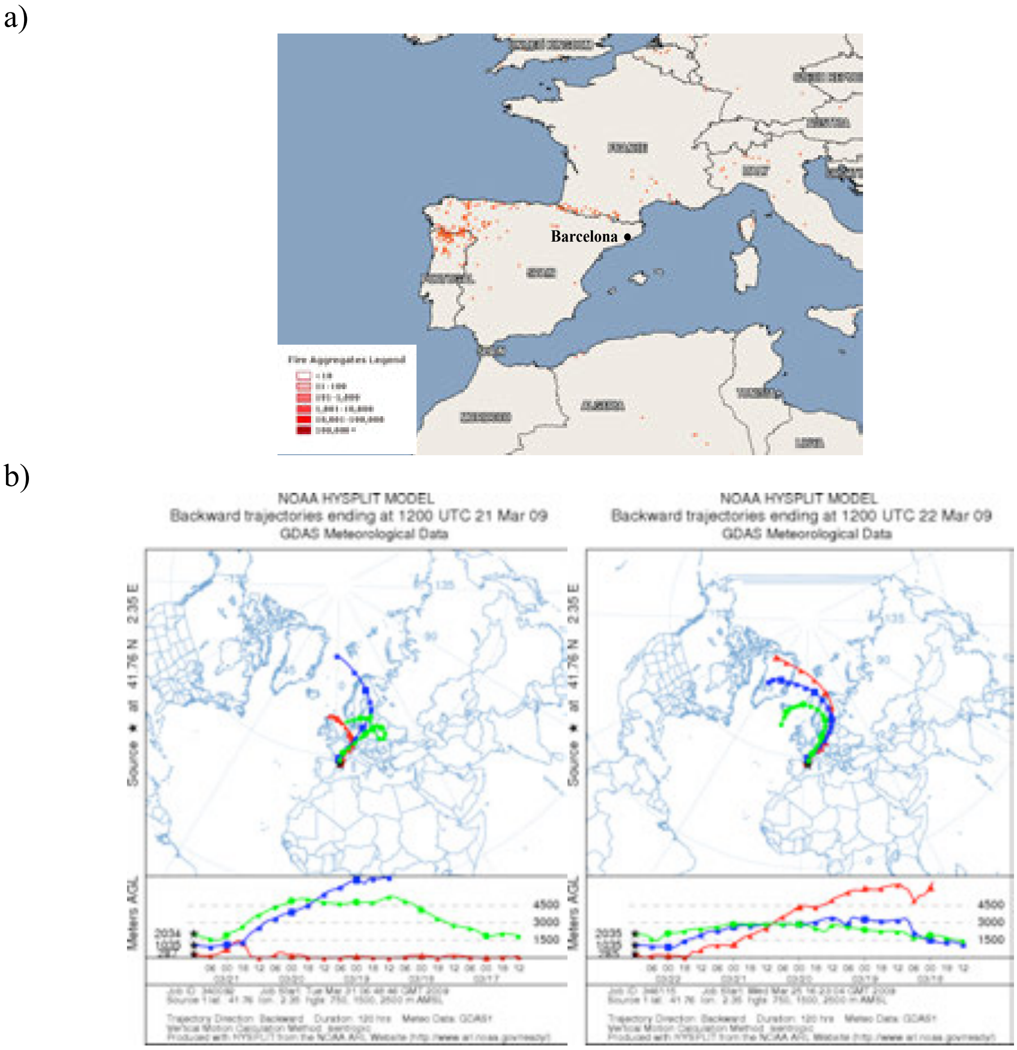

Figure 6.4. a)Web Fire Mapper built by The Fire Information for Resource Management System (FIRMS), indicating the number of fire points during days 20th-23th March of 2009 (http://firefly.geog.umd.edu/firemap/); b)Backtrajectories for days 21st and 22nd March of 2009 (http://ready.arl.noaa.gov/HYSPLIT_traj.php).

6.2.3. Correlation between $PM_{2.5}$ components

The co-variation of $PM_{2.5}$ components was studied in an attempt to understand the variability between day and night emission sources and the relative magnitude of the impact of biomass burning emissions in Barcelona during the DAURE campaign. Thus, correlation of levoglucosan with other aerosol components were calculated distinguishing between day (9:00-21:00h UTC) and night (21:00-9:00h UTC). High correlations were found between levoglucosan and OC (r^2= 0.77) and K^+ (r^2= 0.65) at night (Table 6.4 and Figure 6.5). The correlation was less clear for levoglucosan and EC (r^2= 0.59) or BC (r^2= 0.52) for night time, as most EC is released by fossil sources (Minguillón et al., 2011), but still large differences in the correlation factors between BC and levoglucosan and between EC and levoglucosan were found depending on the time of day (Table 6.4). In general, higher correlations of levoglucosan with major atmospheric pollutants were always found at night, indicating a major importance of this source during this period and lower emissions from other sources. The lack of correlation from 9 to 21h suggests a dilution of biomass burning emissions in the city by vehicle exhaust, resuspension and construction work emissions. In addition to the major impact of these sources during the day, the dilution of pollutants due to a higher altitude of the mixing layer and the development of sea breezes reduce the detectable impact of biomass burning contribution.

It is important to note that though acetonitrile is strongly and predominantly emitted by biomass burning, especially from forest fires (Holzinger et al.,1999), the correlations with levoglucosan was relatively low (r^2=0.53 at night), probably because the emission ratio of acetonitrile to levoglucosan might not be constant. Unfortunately, data on acetonitrile were only available until 20th March, so it was not possible to confirm the above described potential influence of air masses transporting pollutants from distant areas for the 21st-22nd March period. Gaseous pollutants (NO_X and CO) did not show a correlation with levoglucosan at any time, as these compounds are mainly generated by exhaust emissions from local sources. Finally, biomass burning is generally identified by mass fragment 60 measured by AMS (Schneider et al., 2006; Alfarra et al., 2007). Correlation between this parameter and levoglucosan was quite high at night (r^2=0.76) but not during the day period (r^2=0.23) (Table 6.4).

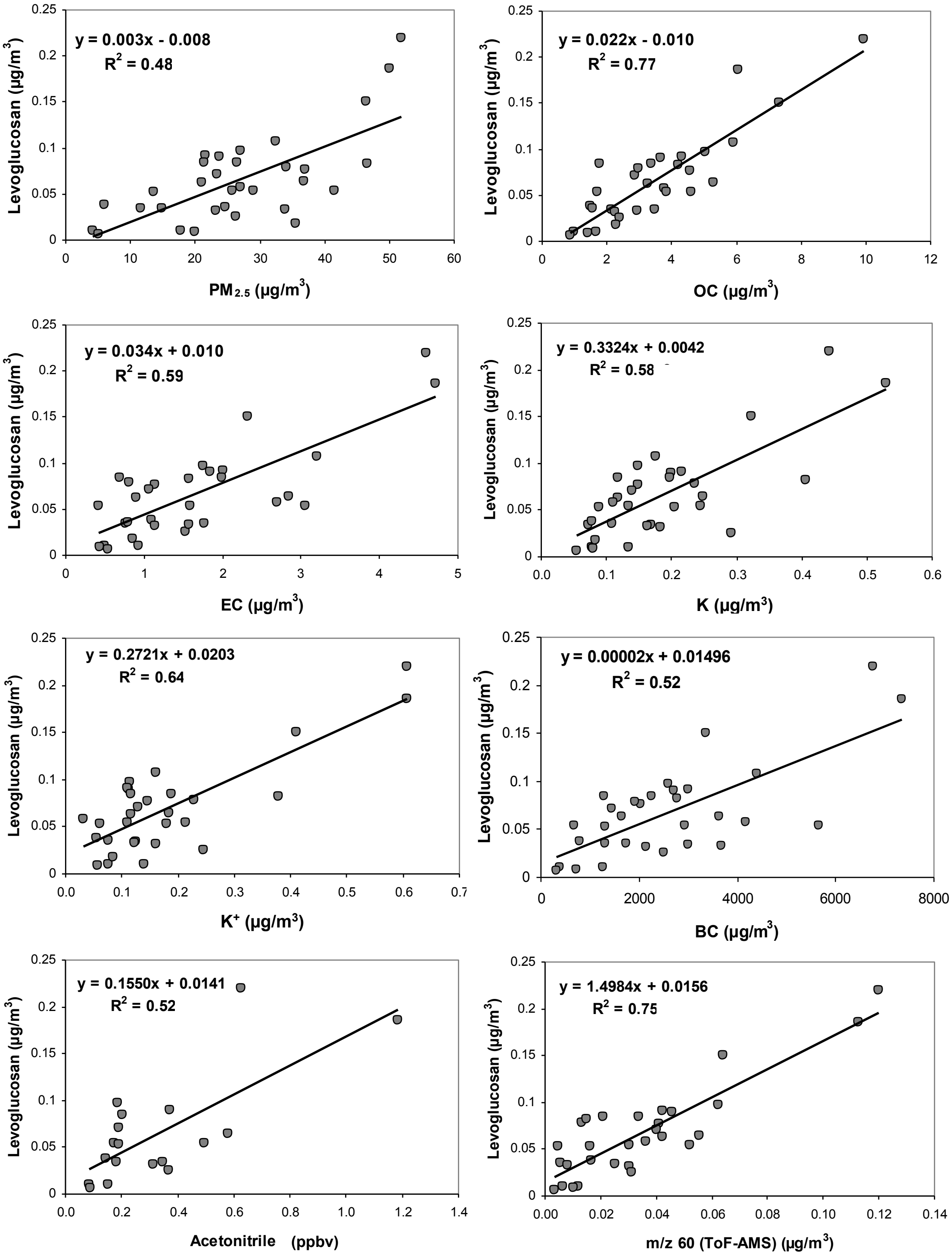

Figure 6.5. Correlations of levoglucosan with major atmospheric parameters at night obtained during the DAURE campaign.

Table 6.4. Correlations of levoglucosan with other aerosol components distinguishing day and night periods during the DAURE campaign.

r^2	Levoglucosan		
	Day	Night	Total
$PM_{2,5}$ (μg/m^3)	0.21	0.49	0.37
OC (μg/m^3)	0.32	0.77	0.64
EC (μg/m^3)	0.11	0.60	0.45
K (μg/m^3)	0.26	0.58	0.45
K^+ (μg/m^3)	0.39	0.65	0.56
BC (μg/m^3)	0.16	0.54	0.41
NOx (μg/m^3)	0.08	0.49	0.37
CO (μg/m^3)	0.05	0.44	0.28
Acetonitrile (ppbv)	0.25	0.53	0.45
***m/z* 60 (ToF-AMS)**	0.23	0.76	0.46

It can be concluded that the impact of biomass burning can be detected by means of suitable tracers even in a complex scenario as the Mediterranean city of Barcelona, with high levels of particulate pollutants mainly caused by primary and secondary emissions from traffic, resuspension, industry, construction works and shipping (Amato et al., 2009a). However, it is important to mention that the number of fires in the north of Spain in March 2009 accounted for an especially high percentage of the average (3800 forest fires in March and a total of around 15000 during the whole year), as recorded in the 10th report on Forest Fires in Europe (2010). Thus, longer time series of biomass burning tracers will be needed to further understand the influence of these emissions from both regional-scale and long-range origins on urban background environments.

6.2.4. Source apportionment

The constrained PMF model provided a nine-factor solution. The model was based on the chemical composition of PM_{10}, $PM_{2.5}$ and PM_1 samples collected throughout 2009; the selected species for the source apportionment analysis were Al, Ca, Fe, K, Mg, Na, S, Mn, Ti, V, Cr, Ni, Cu, Zn, As, Rb, Sr, Cd, Sb, La, Pb, OC, EC, NO_3^-, Cl^-, NH_4^+, K^+ and Levoglucosan, the latter compound was only quantified during the DAURE campaign. A summary evaluation of chemical results is shown in Table 6.5. The solution presented a correlation coefficient (r^2) between the observed and predicted mass concentration of 0.76. The Q-main values (Amato et al., 2009a) for the base and continuation runs were 15021 and 16137 respectively (11019 degrees of freedom), revealing an acceptable increase of 7% due to the constraints introduced to the basic PMF model.

Table 6.5. Summary evaluation of the chemical composition of PM_{10}, $PM_{2.5}$ and PM_1 samples averaged on an annual basis for 2009 including the DAURE campaign.

2009	**PM_{10}**	**$PM_{2.5}$**	**PM_1**
	$\mu g/m^3$		
PM	34.50	22.05	17.68
OC	3.07	2.62	2.18
EC	1.53	1.33	1.12
Al	0.41	0.09	0.03
Ca	1.22	0.22	0.05
Fe	0.54	0.14	0.03
K	0.30	0.16	0.09
Mg	0.26	0.05	0.01
Na	1.06	0.22	0.05
S	1.21	0.95	0.65
NO_3^-	3.09	1.49	0.93
Cl^-	1.34	0.63	0.38
NH_4^+	1.26	1.46	1.17
	ng/m^3		
Ti	26.80	7.67	2.88
V	9.83	8.23	5.66
Cr	3.95	2.23	1.43
Mn	12.76	5.81	2.88
Ni	4.51	3.61	2.54
Cu	25.42	8.67	4.63
Zn	67.71	36.90	21.27
As	0.59	0.43	0.34
Rb	0.77	0.29	0.15
Sr	4.03	1.19	0.38
Cd	0.18	0.16	0.11
Sb	2.49	0.85	0.44
La	0.29	0.12	0.05
Pb	10.00	7.37	4.90
Additional measures for DAURE	**PM_{10}**	**$PM_{2.5}$**	**PM_1**
	$\mu g/m^3$		
Levoglucosan		0.06	
k^+	0.29	0.18	0.14

The nine factors identified contributing to PM_1, $PM_{2.5}$ and PM_{10} during 2009 were vehicle exhaust, secondary nitrate, secondary sulphate, mineral matter, sea salt, fuel oil combustion, industrial processes, road dust and biomass burning. The identification of the biomass burning source was possible only after the use of levoglucosan and K^+ data obtained during the DAURE campaign ($PM_{2.5}$) and of the ratios observed for biomass burning sources reported in Puxbaum et al. (2007) and Caseiro et al. (2009). The PMF model allowed us to extrapolate the source profiles and to obtain the contribution of the nine sources resolved on an annual basis. The nine sources profiles obtained are shown in Figure 6.6.

According to the PMF results, the biomass burning factor was enriched in total K, soluble K, OC and levoglucosan. It explained 84% of the total variation of levoglucosan, 66% of soluble K and 15% of OC. On 2009 annual average basis, it accounted for 5% of PM_1 and 3% of $PM_{2.5}$ and PM_{10} mass. The uncertainty associated with the annual contribution of biomass burning emissions to PM_{10}, $PM_{2.5}$ and PM_1 levels is 45%, 28% and 30%, respectively, according to the analysis described in the methodology section. As expected, contributions are significantly lower than those reported in winter in northern and central European cities (c. 20-45%) (Palmgren et al., 2005). As discussed in previous sections, no source apportionment estimates of biomass burning contributions are currently available for southern European cities for comparison with these results.

Figure 6.7a shows the PMF apportionment of OC during the year 2009 and also within the DAURE campaign for PM_{10}, $PM_{2.5}$ and PM_1. Focusing on the contribution of biomass burning to OC levels, it was 19% (0.6µg m^{-3}), 19% (0.5µg m^{-3}) and 21% (0.4µg m^{-3}) during 2009 for PM_{10}, $PM_{2.5}$ and PM_1, respectively. Similar results were obtained for the DAURE period, in agreement with those described by using other apportionment methods such as ^{14}C (Minguillón et al., 2011) or PMF-AMS (Mohr et al., 2011). The contribution was quite constant among fractions, a result which was unexpected given that biomass burning tracers tend to accumulate in the finer grain size fractions (Saarikoski et al., 2008). However, a limitation of our approach is that the same OC/levoglucosan ratio was applied to all grain sizes. The mean annual contribution of OC from biomass burning to total carbon (TC) was 13, 11 and 13% (18, 17 and 16% in winter) for PM_1, $PM_{2.5}$ and PM_{10}, respectively.

On the other hand, the contribution of biomass burning to soluble K varied greatly among grain sizes, increasing from PM_{10} to PM_1 (Figure 6.7b). The mean annual contribution was 48% (0.08 µg m^{-3}), 79% (0.05 µg m^{-3}) and 94% (0.05 µg m^{-3}) (66%-1.2 µg m^{-3}, 91%-0.9 µg m^{-3} and 97%-0.7 µg m^{-3} during winter) for PM_{10}, $PM_{2.5}$ and PM_1, respectively. Although a large difference was found between the biomass burning contribution to K^+ for the PM_{10} fraction annually and in the winter period, these differences became negligible with decreasing the PM size. Thus, soluble K can be considered an appropriate tracer of biomass burning when considering the fine fraction but one should be cautious when studying PM_{10} data. In fact, as described above, it has been reported that the application of K^+ as a tracer of biomass burning may be quite problematic, as it is influenced by several sources (especially by illitic clays from atmospheric dust) (Querol et al., 2001).

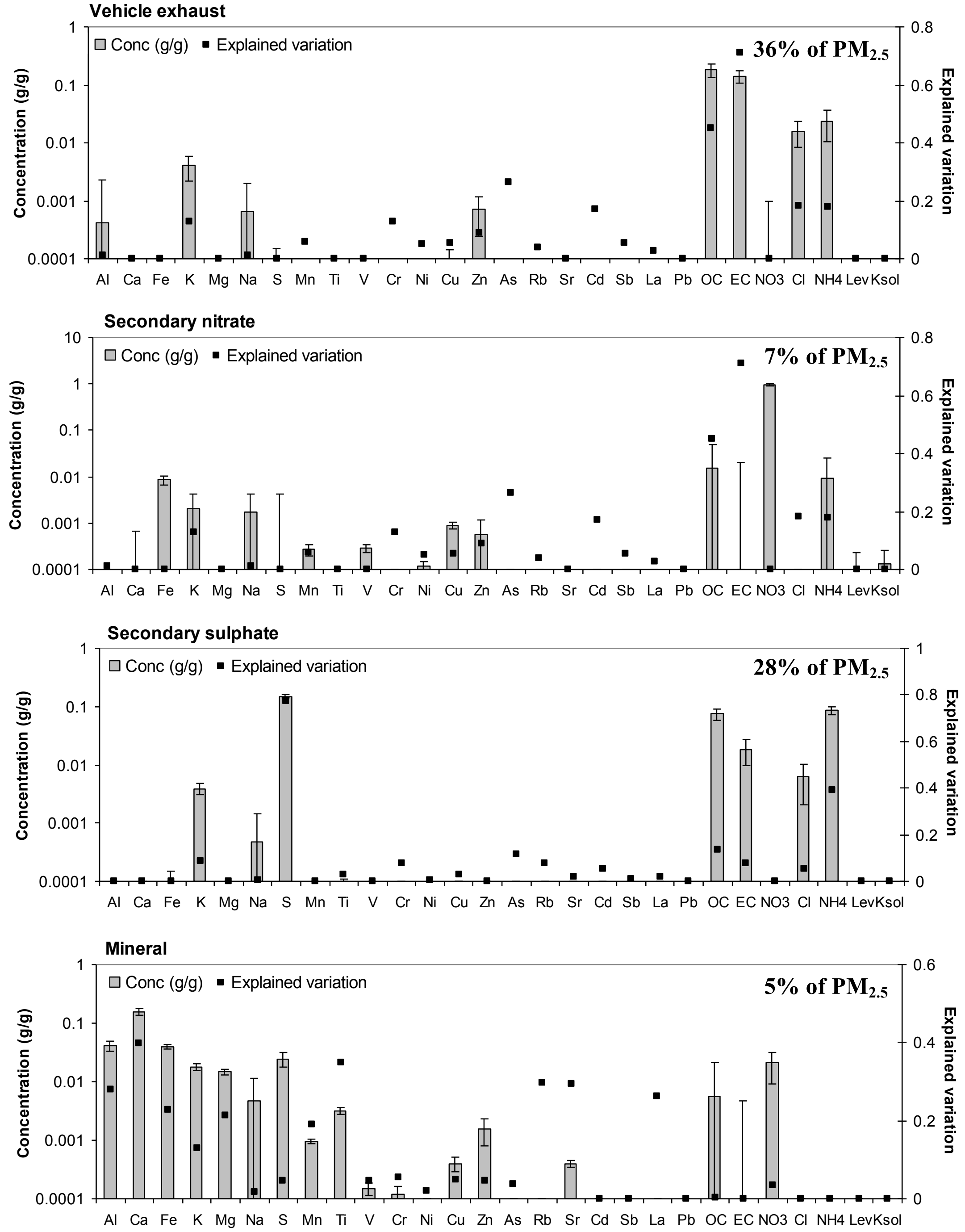

Figure 6.6. PMF sources profiles during 2009. Uncertainties are obtained by bootstrapping replications. The relative contribution to annual mean $PM_{2.5}$ concentration is indicated for each factor.

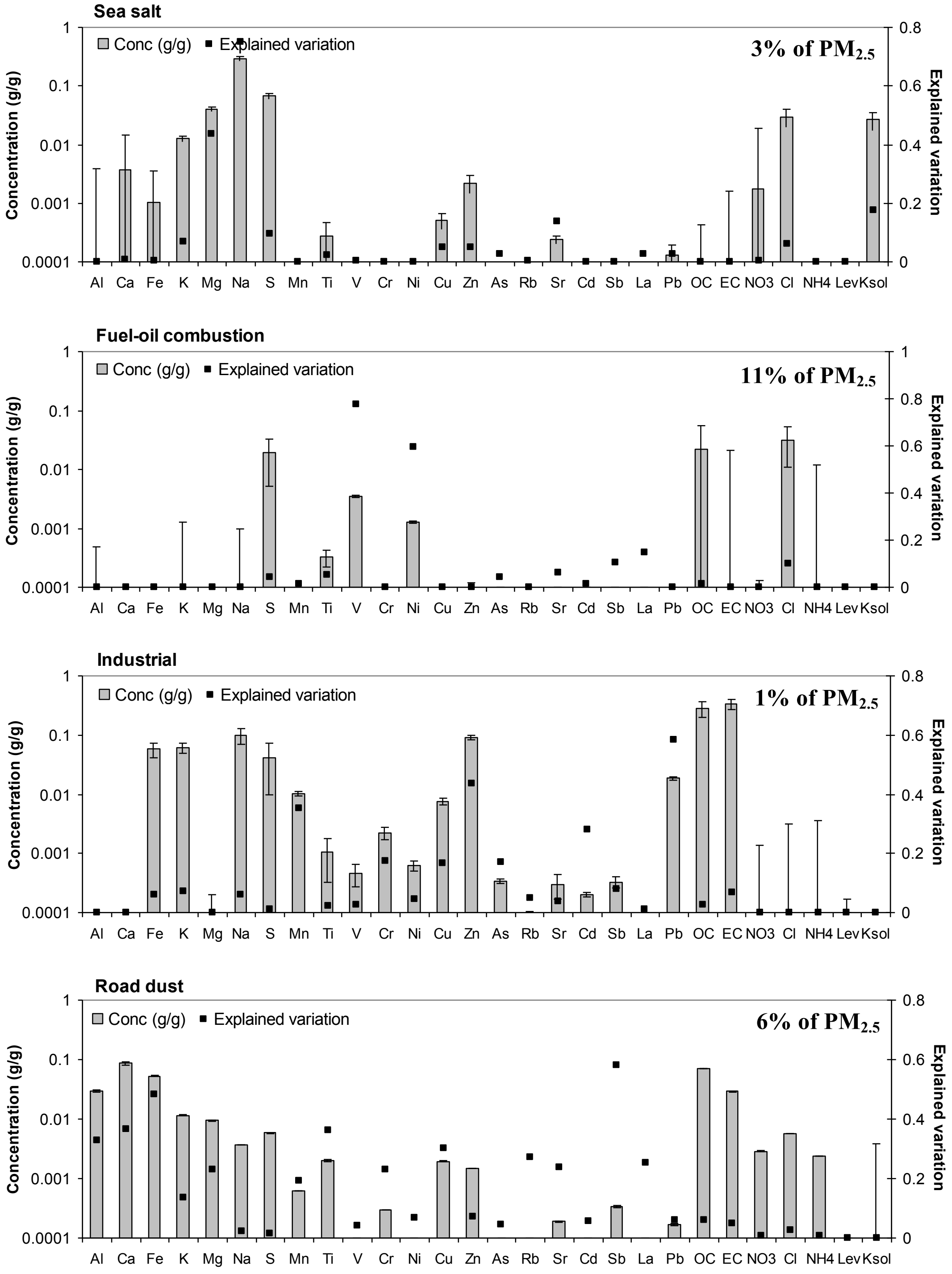

Figure 6.6. Continuation.

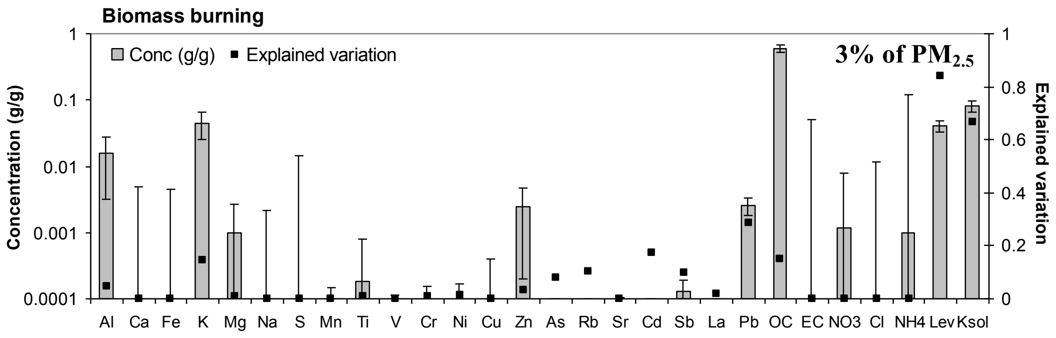

Figure 6.6. Continuation.

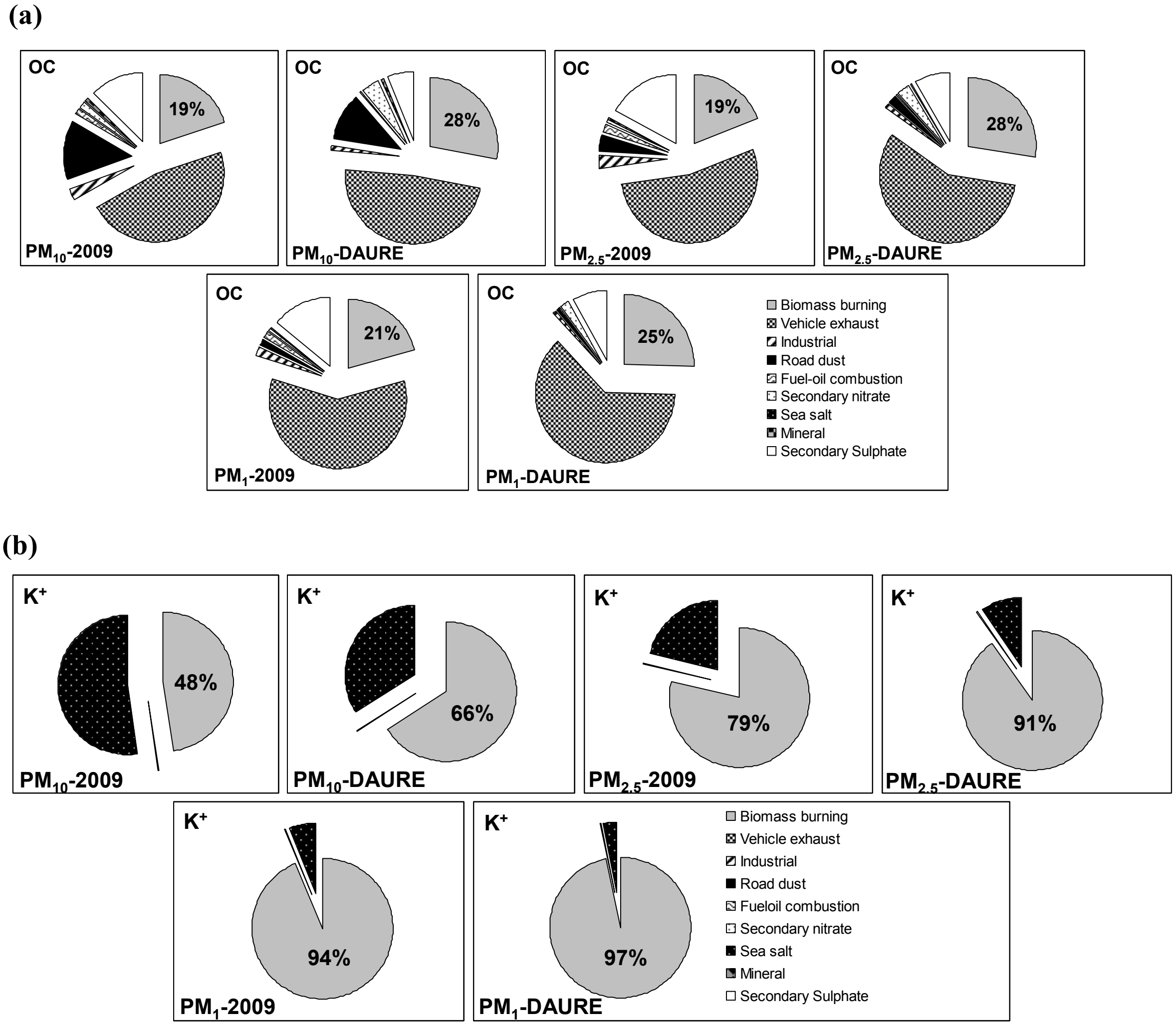

Figure 6.7. Source apportionment to organic carbon (a) and soluble K (b) during 2009 and during the DAURE campaign period for PM_{10}, $PM_{2.5}$ and PM_1 fractions according to the PMF results.

The study of the annual time series of biomass burning contributions (Figure 6.8a) evidenced maxima in winter (February-March) and the summer period. The winter maxima coincided with those shown by levoglucosan levels during the DAURE campaign (Figure 6.2). During the periods of 26-27th February and 12-13th March (under atmospheric stagnation episodes) high contributions from the biomass burning source were estimated (7, 7 and 5% of PM_1, $PM_{2.5}$ and PM_{10}), but also from other combustion and non-combustion sources (mineral, vehicle exhaust), especially from secondary particles in the finer fraction (secondary nitrate and sulphate). Thus, these results confirm the presence of stagnant conditions during these days. During the summer period, the high biomass burning contributions estimated by the model (9, 8, 7% of PM_1, $PM_{2.5}$ and PM_{10}) were interpreted as related to regional-scale agricultural fires and fires occurring in forested areas. It is worthwhile to mention that although the model was able to reflect these summer emissions, levoglucosan levels were below the detection limit for more than 95% of the days, as previously mentioned. This fact could be due to two causes: (a) the questioned stability of levoglucosan under summer conditions since it can be prone to the degradation in the atmosphere and particularly by OH· (Hoffmann et al., 2010, Hennigan et al., 2010), or (b) a limitation of the model when representing this source in summer as the target OC/Levoglucosan ratio of 6.1±0.3 is constant for the whole year.

The contributions from the biomass burning source resolved by the model were not always higher in PM_{10} than in $PM_{2.5}$ and PM_1. This is probably due to the previously mention absence of levoglucosan analysis in PM_{10} and PM_1 samples and consequent "weaker" estimates in PM_{10} and PM_1 than in $PM_{2.5}$ (where the signal of the source is stronger). It is for this reason that the assessment of the mass contributions below is performed for $PM_{2.5}$ only (Figure 6.8).

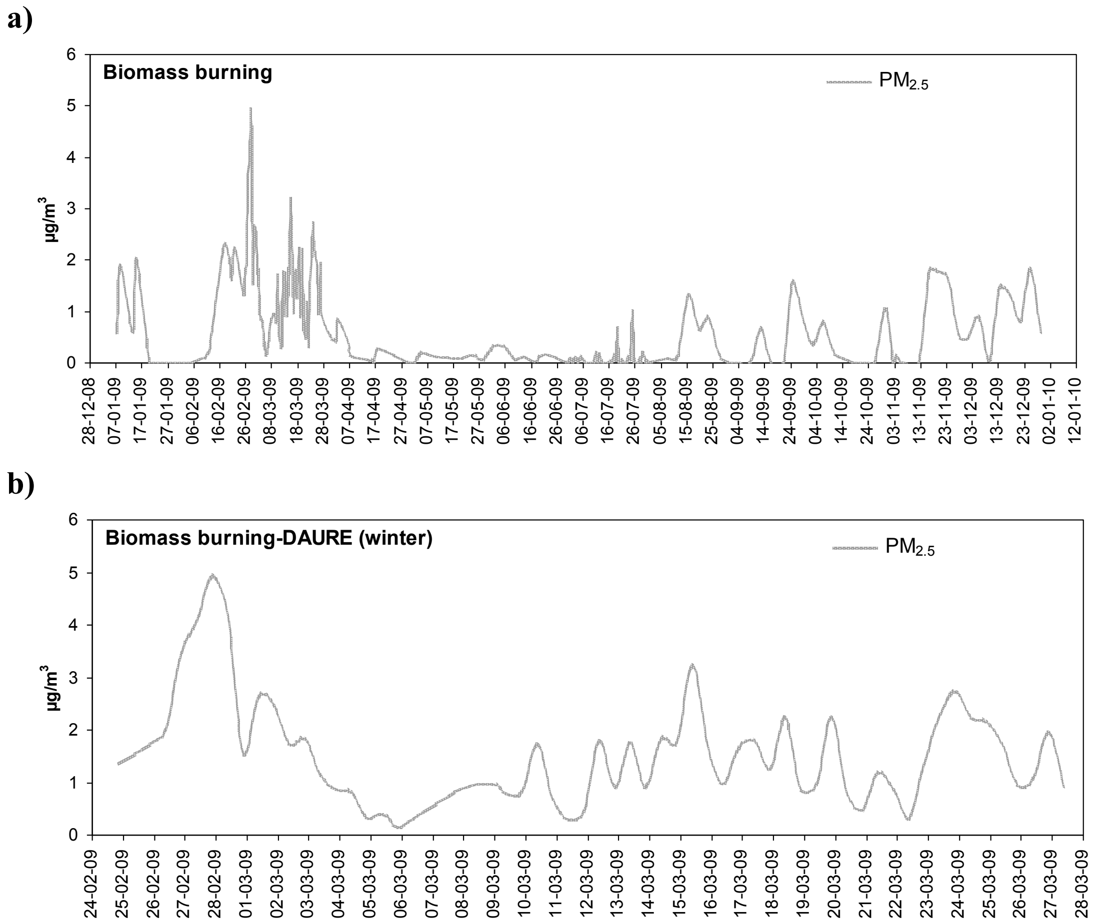

Figure 6.8. Time series of the biomass burning factor obtained by PMF: a) whole year 2009, b) DAURE campaign in winter.

Within the DAURE campaign, the increment of levoglucosan/OC and levoglucosan/$PM_{2.5}$ ratios and the lack of day and night variation allowed identifying the days 21^{st}-22^{nd} March 2009 as days with an important influence of long-range transported biomass burning emissions. This lack of day and night variation is also observed when studying the time series of the biomass burning factor obtained by the PMF analysis (Figure 6.8), especially when analysing the $PM_{2.5}$ fraction, which seems to represent better the biomass burning source. The contribution of biomass burning to $PM_{2.5}$ levels for these days was estimated as 5±1%.

The contribution to $PM_{2.5}$ levels from regional-scale biomass burning emissions was also estimated for the winter period. These contributions were only estimated for the night-time periods (when emissions were detected), and are not expressed as daily mean values given the day-time dilution derived from other sources and the increment of the mixing layer height. This contribution was calculated as the mean increment of biomass burning contributions during night with respect to the day period, in the $PM_{2.5}$ fraction, for days with a marked day-night oscillation of the biomass burning source contributions (1st, 2nd, 10th, 12th, 13th, 15th, 16th, 19th, 23rd and 26th March). On average, the contribution from the biomass burning source due to regional sources accounted for 3±1% of $PM_{2.5}$. As discussed above, the estimation was based on $PM_{2.5}$ levels in order to limit uncertainties, as the model seems to represent biomass burning emissions more accurately in this particle size, possibly due to the fact that levoglucosan levels (one of the main tracers of this source) were only analysed in this fraction. A characteristic levoglucosan/OC ratio of the biomass burning aerosols of 0.015±0.010 was obtained for regional-scale biomass burning sources.

6.3. CONCLUSIONS

The impact of biomass burning emissions was detected at an urban background site in Barcelona by means of levoglucosan, K^+ and OC concentrations despite the complexity of the source mixture affecting the air quality of the city, characterised by notable primary and secondary traffic emissions.

Levoglucosan levels obtained in Barcelona were lower than in urban environments in northern and central European regions, indicating that biomass burning habits and conditions differ widely among EU regions.

In winter, a high correlation between levoglucosan and OC (r^2= 0.77) and K^+ (r^2=0.65) in $PM_{2.5}$ was found at night. A higher ratio of levoglucosan with major atmospheric pollutants was always found at night, suggesting the transport of biomass burning emissions from the regional scale towards the city and also a lower impact of major urban sources during this period. The lack of correlation from 9 to 21h UTC points to a dilution of this source in the city during day-time, when exhaust emissions, re-suspension and construction works are the main causes of air quality degradation. For specific days (21-22 March), the contribution from long-range transported biomass burning aerosols was detected in Barcelona, by increased levoglucosan/OC ratios which did not follow the typical day-night variability described above. The characteristic ratio for long-range transported biomass burning aerosols was levoglucosan/OC=0.05±0.01 in this study. For regional-scale biomass burning sources, the levoglucosan/OC ratio obtained was 0.015±0.010.

The quantification of the annual mean biomass burning contribution to PM levels was possible by means of the PMF (ME-2) model, introducing constraints regarding upper limits for ammonium and K^+, a lower limit for OC and a target OC/levoglucosan ratio of 6.1±0.3. On an annual basis, biomass burning emissions accounted for 3% of the annual PM_{10} and $PM_{2.5}$ concentrations, increasing to 5% in the case of PM_1. During the winter period of the DAURE intensive campaign, the contributions from regional-scale biomass burning sources accounted for 3±1% of $PM_{2.5}$ during night-time periods, when emissions were detected. These emissions possibly originated by agricultural waste burning and transported towards Barcelona by night-time land breezes. On the other hand, the contribution from long-range transported biomass burning emissions was estimated in 5±1% of $PM_{2.5}$ for a specific episode (possibly originating from forest or agricultural fires).

On an annual basis, the contribution of biomass burning emissions to OC concentrations was unexpectedly constant among PM fractions and higher during winter (25-28%). On the other hand, the contribution to K^+ increased significantly from PM_{10} to PM_1 (48-94%). Results evidenced that K^+ from biomass burning is mostly emitted in the fine fraction and coarse K^+ should not be taken as an appropriate tracer of biomass burning.

ACKNOWLEDGEMENTS

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CHAPTER 7: A multidisciplinary approach to characterise exposure risk and toxicological effects of PM_{10} and $PM_{2.5}$ samples in urban environments

Parts of the results presented within this chapter have been published in Ecotoxicology and Environmental Safety, 78, 327-335, 2012: A multidisciplinary approach to characterise exposure risk and toxicology of PM_{10} and $PM_{2.5}$ in urban environments. Authors:

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7. A MULTIDISCIPLINARY APPROACH TO CHARACTERISE EXPOSURE RISK AND TOXICOLOGY OF PM_{10} AND $PM_{2.5}$ IN URBAN ENVIRONMENTS

ABSTRACT

Urban aerosol samples collected in Barcelona during 2008 and 2009 were toxicologically characterized by means of two complementary methodologies allowing evaluation of their Reactive Oxidative Stress (ROS)-generating capacity: the plasmid scission assay (PSA) and the dichlorodihydrofluorescin assay (DCFH). The PSA determined the PM dose able to damage 50% of a plasmid DNA molecule (TD_{50} values), an indication of the ability of the sample to exert potential oxidative stress, most likely by formation of ·OH. This toxicity indicator did not show dependency on different air mass origins (African dust, Atlantic advection), indicating that local pollutant sources within or near the city are most likely to be mainly responsible for PM health effect variations. The average TD_{50} values show $PM_{0.1\text{-}2.5}$ samples to be more toxic than the $PM_{2.5\text{-}10}$ fraction, with doses similar to those reported in previous studies in polluted urban areas. In addition, the samples were also evaluated using the oxidant-sensitive probe DCFH confirming the positive association between the amount of DNA damage and the generation of reactive oxidant species capable of inducing DNA strand break. Results provided by the PSA were compared with those from two other different methodologies to evaluate human health risk: 1) the toxicity of particulate PAHs expressed as the calculated toxicity equivalent of benzo[a]pyrene (BaPteq) after application of the EPA toxicity factors, and 2) the cancer risk assessment of the different PM sources detected in Barcelona with the receptor model Positive Matrix Factorization (PMF) and the computer program Multilinear Engine 2 (ME-2) using the organic and inorganic chemical composition of particles. No positive associations were found between PSA and the toxicity of PAHs, probably due to the inefficiency of water in extracting organic compounds. On the other hand, the sum of cancer risk estimates calculated for each of the selected days for the PSA was found to correlate with TD_{50} values in the fine fraction. Further studies are necessary to determine whether the higher toxicity of $PM_{0.1\text{-}2.5}$ samples compared to $PM_{2.5\text{-}10}$ samples is related to PM chemical composition and sources, or rather to its size distribution.

Keywords: PM, ROS, toxicology, risk assessment, source apportionment

7.1. INTRODUCTION

There is consistent evidence that current levels of atmospheric particulate matter (PM) are associated with increasing mortality and morbidity among urban populations (Pope et al., 2008; Greenwell et al., 2002). Much recent attention has been focused on the size and composition characteristics of these particles, as well as on toxicological mechanisms using exposure experiments and population-based epidemiology.

Transition metals may represent a major determinant of the toxicity of PM (Aust et al., 2002). Cahill et al. (2011) found a causal relationship between the reduced vanadium and nickel concentrations in the California Central Valley and the improved ischemic heart disease rate. Some metals can stimulate the generation of (•OH) by Fenton-type reactions (Valavanidis et al., 2000), these free radicals can then induce damage to the genetic material. Becker et al. (2005) performed principal-component analysis (PCA) in order to assess the effect of particles constituents in the potency for PM to induce Reactive Oxygen Species (ROS) production and found a factor comprising Zn, As, V, Ni and Pb associated with ROS end points. Chemicals in the fine PM having notable impact on human health include not only transition metals but also organic compounds, such as polycyclic aromatic hydrocarbons (PAHs). Products resulting from the metabolic activation of PAHs can enter redox cycling and consequently generate ROS (Burczynski and Penning, 2000).

How the ROS-stimulating potential of PM may be linked to increased mortality is unclear (Wang et al., 2010; Wei et al., 2011), but it seems likely that the contribution of factors other than purely elemental composition would need to be considered.

One of the mechanisms that have been commonly proposed to explain the association of PM exposure and occurrence of respiratory infections, lung cancer, and chronic cardiopulmonary diseases is the oxidative DNA damage through the generation of ROS. It has been argued that oxidative stress is an important toxicological mechanism of particle induced lung cancer (Knaapen et al., 2004; Risom et al., 2005). The biochemical pathways leading to cell damage involve both non-cellular characteristics of particles (including shape, size, solubility, surface reactivity, carrier function, and surface chemistry) and cellular properties (including the ability of generating ROS, alteration of signalling pathways, and initiation of inflammation) (Knaapen et al., 2004; Møller et al., 2008).

ROS assay strategies have been applied in different scientific fields in order to establish provisional classification criteria for risk assessment of pollutants toxicity

(Onoue et al., 2008). Recent epidemiologic, toxicological, and controlled human exposure studies have evaluated the health effects associated with PM sources using risk assessment of air pollutants applied to a broad set of components (Stanek et al., 2011 and references therein). In them, the additional risk of developing cancer due to continuous exposures to carcinogenic compounds is calculated as the product of unit risk and the exposed concentration (USEPA, 2005). However, the compounds-specific risks estimates provide only limited information for source air quality management, due to contributions from multiple sources for each compound (Wu et al., 2009). Thus, Mukerjee and Biswas (1992) made an initial demonstration of the efficiency of this estimation by using a Chemical Mass Balance model to apportion six samples of total suspended PM collected at a residential site near several industrial sources. These authors calculated source-specific risks by summing the species-specific risks for each source profile including paved road dust ($7.5x10^{-5}$), blast furnace ($6.8x10^{-6}$) and sinter plants ($3.4x10^{-5}$). Recent studies have estimated source-specific lifetime excessive cancer risk of selected air pollutants in urban environments with an emphasis on health risk of the PM using the Multilinear Engine (ME-2) model in US (Wu et al., 2009), as well as on indoor aerosols in China (See et al., 2005).

The main objective of this work is to characterize the toxicological effects of PM_{10} and $PM_{2.5}$ samples in an urban environment applying two different assays: the Plasmid Scission Assay (PSA) and the Dichlorodihydrofluorescin assay (DCFH), two complementary and easily adapted techniques for the elucidation of PM-ROS generating capacity. It is expected to observe differences in bioreactivity based on three main factors: (1) PM size fraction, (2) local pollution sources and (3) meteorological conditions. In addition, source-specific concentrations of PM_{10}, $PM_{2.5}$ and PM_1 were calculated using the Positive Matrix Factorization (PMF) receptor model with the Multilinear Engine 2 (ME-2) scripting, introducing organic (PAHs) and inorganic chemical compounds, and thus source-specific lifetime excessive cancer risks of PM in an urban site in Barcelona were estimated. The source apportionment analysis has been described in detail in chapter 2, section 2.4.2. We attempt a correlation between results from the toxicological assays and those from the risk assessment in order to compare methodologies.

To achieve the objectives above a sampling campaign was carried out at the IJA urban background site. The specifications of the sampling routine and subsequent chemical analysis are detailed in chapter 2 in the section defined as “Urban aerosols bioreactivity evaluation (2008-2009)”.

7.2. RESULTS AND DISCUSSION

A comparison between PM samples collected in quartz filters and PUFs confirms a good correlation between the two methods (Figure 7.1). Variations in PM concentrations between three atmospheric scenarios demonstrate a strong influence of NAF episodes (North African Saharan intrusion) on PM_{10} concentrations which rise up to 82 µg m^{-3} (Table 7.1). During UP episodes (local pollutant accumulation under stagnant conditions), concentrations are elevated in all three grain-sizes (maximum of 47.4 µg m^{-3} PM_{10}, 25.6 µg m^{-3} $PM_{2.5}$ and 16.6 µg m^{-3} PM_1), whereas during cleansing AT episodes (Alantic advection) PM concentrations of PM_{10}, $PM_{2.5}$ and PM_1 decrease to 28.7, 14.8 and 7.5 µg m^{-3} respectively.

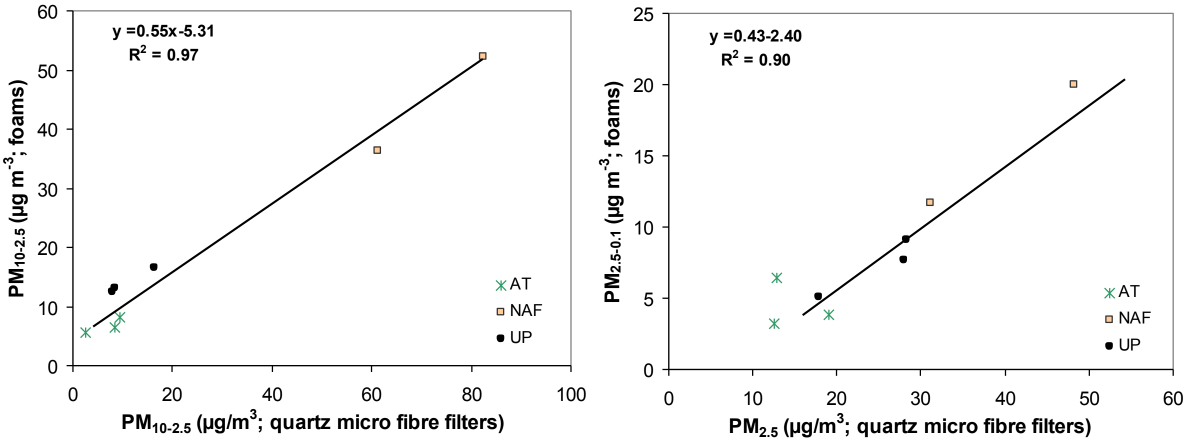

Figure 7.1. Correlations between PM concentrations from quartz filters and those obtained from foams distinguishing the different scenarios.

Table 7.1. Chemical composition of PM_{10}, $PM_{2.5}$ and PM_1 for each of the different scenarios during the sampling period (AT: Atlantic Advection, NAF: North African Saharan intrusion, UP: Local pollutant accumulation under stagnant conditions). It is important to note that $PM_{2.5}$ and PM_1 quartz fibre filter samples were collected until December 2008, whereas PM_{10} samples were collected until December 2009.

	PM_{10}			**$PM_{2.5}$**			**PM_1**		
	AT	**NAF**	**UP**	**AT**	**NAF**	**UP**	**AT**	**NAF**	**UP**
Number of days	12	4	4	3	2	3	3	2	3
%									
Mineral	31	47	32	19	40	24	5	5	5
Sea salt	4	4	4	2	1	1	2	1	1
[1]SIC	12	19	21	23	28	29	19	40	31
[2]OM+EC	30	15	25	35	21	41	62	48	44
Trace metals	1.0	0.7	1.0	0.5	0.6	1.1	1.2	0.7	0.8
Total PM ($\mu g\ m^{-3}$)	28.7	82.4	47.4	14.8	40.2	25.6	7.5	14.8	16.6

7.2.1. PM composition

-Inorganic fraction

Overall, around one third of the PM_{10} fraction comprises mineral dust (Al_2O_3 + SiO_2 + CO_3^{2-} + Ca + Mg + K + Fe = 32% on average), with lesser amounts of sea spray (Na^+ + Cl^- = 4%), NH_4^+–Ca–K–Mg sulfate and NH_4^+–Na–Ca nitrate species (17%) and Organic Matter (OC*1.7) and Elemental Carbon (EC) (OM+EC=22%), with a OM/EC ratio of 2.4. Lower concentrations of Na, Cl, Al, Ca, and Mg occur in the $PM_{2.5}$ fraction, although the mineral load was still relatively high (25%) due to the influence of primary PM emissions at urban sites (Amato et al., 2009a). It is important to note that given the great impact of construction works during the year 2008 and the presence of NAF outbreaks, the contribution of mineral matter was extremely high during the selected days.

The percentage of carbonaceous components and secondary inorganic compounds in this finer size fraction increased up to 36% and 21%, respectively. The mineral matter load in PM_1 was much less (5%), this fraction being predictably mostly made up of OM and EC (51%), with a OM/EC ratio of 2.2, and secondary inorganic aerosols (30%).

Table 7.1 shows the chemical composition of each PM fraction for the three types of air masses, and highlights the high mineral load in the NAF PM_{10} and $PM_{2.5}$ fractions (47 and 40% respectively), and the high UP levels of secondary inorganic compounds and carbonaceous material. Sea salt levels are low and similar for all three episodes. Contributions of trace metals to PM mass do not follow a clear pattern among different episodes and the behaviour is different for each grain size. Figure 7.2 shows a comparison of trace metal levels during the selected days for toxicological characterization with those analysed in other urban background stations in Spanish cities (see Table 7.2 for further information about trace metals levels). Only those metals in the upper limit of the range or above are represented. It is clear that metals with relative high concentrations in the PM_{10} and/or $PM_{2.5}$ Barcelona samples are those directly related with fuel-oil combustion (V, Ni), road dust (Cu, Ba, Sn and Sb), industrial emissions (Cr, Zn, As) and mineral matter (Ba, Bi, Ce, La, Li, Se, Sr, Tl, Th, Rb).

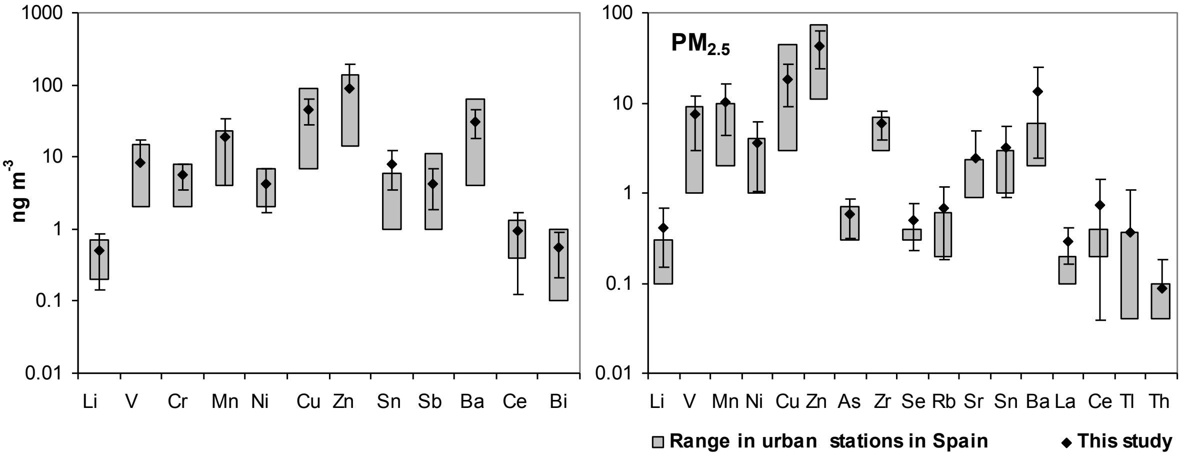

Figure 7.2. Comparison of average trace metals levels during the selected days for toxicological characterization with those registered in other urban background stations in Spanish cities (Querol et al., 2007).

Table 7.2. Trace metals composition of PM_{10}, $PM_{2.5}$ and PM_1 for days characterized by bioreactivity assays.

PM_{10} (ng m^{-3})

Date	1-10-08	7-10-08	16-10-08	22-10-08	4-11-08	18-11-08	11-12-08	19-3-09	22-4-09	24-5-09	5-6-09	17-6-09	29-6-09	28-9-09	19-10-09	30-10-09	11-11-09	19-11-09	9-12-09
Li	0.6	0.8	3.3	0.4	0.5	0.6	0.3	1.5	1.1	2.1	0.5	1.0	1.2	0.7	0.5	0.6	1.0	0.9	0.7
P	33.4	39.2	105.2	25.6	23.7	28.6	12.1	55.5	60.1	57.4	36.8	57.7	49.7	27.4	18.9	22.0	31.1	30.0	21.7
Ti	36.7	49.3	287.4	33.1	33.9	50.3	22.5	90.8	75.2	188.9	41.0	75.2	78.5	49.1	32.9	38.3	60.5	71.6	48.8
V	5.7	6.2	19.7	5.8	3.7	8.1	3.7	17.4	12.9	13.7	17.0	38.4	17.8	3.9	10.9	9.8	5.3	14.5	8.9
Cr	4.4	3.1	9.3	3.0	5.0	8.5	7.4	9.2	10.8	8.5	6.9	7.1	7.6	8.3	8.2	6.9	12.0	9.0	13.7
Mn	13.5	21.5	60.1	13.0	13.8	21.5	19.0	32.8	30.2	37.5	17.8	23.8	33.9	27.6	18.3	18.4	70.5	33.7	51.6
Co	0.2	0.3	1.2	0.3	0.2	0.3	0.3	0.5	0.5	0.8	0.3	0.6	0.5	0.4	0.3	0.3	0.7	0.5	0.5
Ni	2.4	2.8	9.4	2.6	2.7	4.0	1.9	7.1	6.0	6.2	5.8	13.8	6.1	3.4	5.5	5.0	4.6	7.2	6.3
Cu	49.7	38.4	69.9	41.4	68.7	69.2	63.7	78.6	70.2	49.6	40.8	68.7	71.8	69.6	61.5	51.4	101.3	67.8	99.5
Zn	40.4	50.9	38.9	70.9	21.6	89.1	69.8	89.1	203.1	36.7	114.6	70.6	306.5	49.5	73.0	57.5	322.8	73.5	238.4
As	0.6	0.7	1.5	0.5	0.9	0.8	0.5	1.3	1.7	0.9	0.7	0.8	1.3	1.0	0.7	0.9	1.6	1.0	1.0
Se	0.7	0.8	1.2	0.3	0.4	0.3	0.2	2.3	1.3	0.8	0.8	0.5	1.2	0.6	0.5	0.5	0.5	0.8	0.8
Rb	0.9	1.3	4.9	0.6	0.8	1.1	0.5	2.5	1.9	3.4	0.9	1.8	2.0	1.4	0.9	1.1	1.7	1.6	1.2
Sr	4.0	5.3	24.8	3.0	3.7	4.3	2.0	9.9	7.3	19.6	5.4	7.7	9.0	4.1	4.5	3.8	7.0	6.6	5.9
Cd	0.1	0.1	0.2	0.2	0.5	0.3	0.1	0.4	0.5	0.2	0.3	0.3	0.5	0.5	0.2	0.3	0.6	0.4	0.4
Sn	7.3	3.9	6.7	4.5	12.2	11.5	7.0	13.5	18.3	7.4	7.2	11.0	11.7	10.0	10.9	9.7	16.7	9.8	21.2
Sb	4.2	2.6	4.9	2.7	4.6	6.9	3.1	10.7	8.0	4.4	3.1	7.1	7.4	6.4	6.2	6.2	9.8	6.8	11.7
Ba	16.3	4.9	5.0	11.2	78.1	25.1	14.3	15.1	38.7	41.8	36.2	57.4	47.3	24.7	21.7	20.1	26.4	16.7	26.1
La	0.3	0.4	2.2	0.3	0.3	0.4	0.2	0.8	0.7	1.5	0.4	0.9	0.8	0.5	0.3	0.4	0.5	0.6	0.4
Ce	0.7	0.9	5.6	0.7	0.8	1.0	0.5	1.7	1.6	3.8	0.9	1.7	1.8	1.1	0.8	0.9	1.5	1.4	1.2
Tl	0.28	0.14	0.20	0.04	0.07	0.10	0.06	0.15	0.15	0.09	0.07	0.03	0.44	0.05	<D.L.	0.04	0.09	0.05	0.09
Pb	7.2	12.4	13.3	7.8	12.7	14.1	8.8	16.0	18.2	6.5	18.2	8.7	20.4	9.5	9.6	8.2	31.0	13.9	18.6
Bi	0.5	0.4	0.4	0.5	0.7	0.7	0.5	0.9	0.9	0.4	0.3	0.7	2.4	0.6	0.5	0.5	0.9	0.6	0.8
Th	0.10	0.15	0.77	0.05	0.14	0.14	0.06	0.01	0.23	0.56	0.10	0.21	0.23	0.10	0.07	0.04	0.13	0.14	0.08
U	0.02	0.05	0.23	0.04	0.10	0.06	0.02	0.17	0.12	0.18	0.05	0.06	0.06	0.07	0.005	0.01	0.003	0.003	0.04

$PM_{2.5}$ (ng m^{-3})

Date	1-10-08	7-10-08	15-10-08	16-10-08	22-10-08	4-11-08	18-11-08	11-12-08
Li	0.2	0.2	1.1	0.9	0.2	0.4	0.2	0.1
P	13.8	15.8	46.6	31.5	14.5	16.9	14.8	3.7
Ti	1.0	1.3	7.9	6.1	13.9	24.2	14.4	6.6
V	5.4	4.0	16.0	10.8	4.0	2.4	4.7	2.6
Cr	1.8	0.7	3.5	3.1	0.6	2.1	2.9	4.8
Mn	6.8	10.1	25.0	13.3	6.6	8.1	9.8	11.2
Co	0.1	0.1	0.6	0.4	0.1	0.1	0.1	0.1
Ni	2.0	1.6	9.2	5.0	1.9	1.5	2.4	1.3
Cu	26.2	18.6	47.0	25.4	22.3	37.7	35.5	31.7
Zn	33.1	35.7	83.3	44.8	67.7	37.6	67.9	58.1
As	0.5	0.4	1.2	0.9	0.4	0.8	0.6	0.4
Se	0.6	0.7	0.9	0.8	0.3	0.4	0.2	0.2
Rb	0.4	0.4	1.9	1.4	0.3	0.6	0.4	0.2
Sr	1.3	1.2	7.4	5.9	1.1	1.9	1.0	0.6
Cd	0.2	0.1	0.3	0.1	0.2	0.5	0.3	0.1
Sn	3.7	1.7	4.6	1.9	2.0	8.9	5.9	3.8
Sb	2.0	1.0	2.4	1.5	0.8	2.1	2.5	1.2
Ba	6.7	2.3	12.9	37.4	18.6	21.1	4.8	6.5
La	0.1	0.1	0.8	0.7	0.1	0.2	0.1	0.1
Ce	0.4	0.3	2.1	1.7	0.4	0.6	0.4	0.2
Tl	0.12	0.09	2.18	0.16	0.03	0.05	0.08	0.04
Pb	6.9	9.8	17.6	10.3	6.3	11.3	12.6	7.9
Bi	0.4	0.2	0.3	0.2	0.3	0.5	0.4	0.2
Th	0.05	0.04	0.24	0.24	0.01	0.08	0.03	0.02
U	0.04	0.03	0.04	0.11	0.04	0.05	0.05	0.01

PM_1 (ng m^{-3})

Date	1-10-08	7-10-08	15-10-08	16-10-08	22-10-08	4-11-08	18-11-08	11-12-08
Li	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
P	1.8	7.1	9.9	8.7	7.7	5.3	7.0	2.3
Ti	2.6	4.9	5.1	5.1	2.7	1.5	2.4	3.7
V	3.3	2.9	8.8	6.4	2.8	0.8	2.3	2.9
Cr	1.0	0.3	0.5	0.4	1.6	0.2	5.7	4.0
Mn	2.3	4.8	5.9	2.0	3.6	1.7	4.8	10.9
Co	0.06	0.05	0.17	0.09	0.05	0.02	0.06	0.19
Ni	1.4	1.4	5.2	3.8	1.9	0.7	5.1	1.6
Cu	5.3	5.6	11.5	5.6	5.9	5.2	13.0	15.4
Zn	24.8	16.1	26.6	28.7	62.4	14.7	118.5	62.6
As	0.3	0.3	0.7	0.4	0.3	0.3	0.6	0.6
Se	0.3	0.5	0.1	0.3	0.2	0.2	0.2	0.4
Rb	0.1	0.2	0.3	0.2	0.1	0.1	0.4	0.3
Sr	0.4	0.3	0.4	0.4	0.6	0.1	1.4	0.2
Cd	0.1	0.1	0.2	0.1	0.1	0.3	0.3	0.1
Sn	1.6	0.9	2.2	0.7	1.1	2.5	3.1	3.9
Sb	0.6	0.4	0.8	0.5	0.7	0.4	0.8	0.6
Ba	72.8	42.7	40.6	15.6	60.0	6.2	2.2	4.9
La	0.05	0.05	0.05	0.07	0.06	0.04	0.05	0.07
Ce	0.2	0.1	0.2	0.2	0.2	0.1	0.2	0.2
Tl	0.04	0.06	1.53	0.12	<D.L.	<D.L.	0.06	<D.L.
Pb	4.5	6.5	9.0	6.4	5.4	4.2	9.2	10.8
Bi	0.2	0.1	0.1	0.1	0.2	0.1	0.2	0.2
Th	0.05	0.03	0.02	0.02	0.03	0.002	<D.L.	0.02
U	0.07	0.04	0.03	0.01	0.06	0.02	0.01	0.04

- *Polycyclic Aromatic Hydrocarbons*

Table 7.3 shows the average concentrations and the standard deviation values of carcinogenic PAHs analysed in the quartz fibre filters. It is important to note that in the case of $PM_{2.5}$ and PM_1 results were only available for 8 days, whereas 20 samples were obtained for PM_{10}. Considering days with all 3 fractions available for PAH analysis, it can be concluded that PAH are predominantly present in the fine particles (PM_1) and that there is no significant contribution from coarse particles ($PM_{2.5\text{-}10}$) to these compounds. From this, we deduced that the information given by the PM_{10} fraction can also describe and be used to interpret the concentrations of these compounds in the PM finest fractions of the urban environment of Barcelona.

For most of the PAHs, levels are lower than those reported in recent studies in Europe (van Drooge et al., 2009b; Dvorská et al., 2011). Similar levels of benzo[k]fluoranthene and benzo[a]pyrene were found in Zaragoza (Spain, Callén et al., 2011), while benzo[a]pyrene concentrations were also in the same range that in Vegorities (Greece, Terzi et al., 2004). No high correlations between the origin of the air masses and concentration of specific PAHs, or the sum of them, have been found, leading us to conclude that local sources seem to be the main control on variations in the PAH concentrations.

The average PAH profile is very similar between the samples, with highest contributions found for benzo[e]pyrene and benzo[ghi]perylene, followed by chrysene (+thriphenylene). In order to identify possible PAH emission sources, ratios of isomers have been widely used (Rogge et al., 1993; Dvorská et al., 2011). However, after emission the PAH mixtures are exposed to photo-oxidants such as O_3, OH and NO_2 that react with some of these compounds modifying their relative composition (Esteve et al., 2006). Although association of PAH compounds to particles may partially protect them from photo-oxidation (Esteve et al. 2006), caution should be taken when using the ratios of isomers as a source apportionment tool (Galarneau, 2008). With this in mind the ratios of isomers in the PM in Barcelona are very similar among all analyzed samples; Phe/(Phe+Ant) = 0.91 ± 0.02; BaA/(BaA+Chr+Tri) = 0.32 ± 0.03, and IP/(IP+BgP) = 0.29 ± 0.07, indicating that source emissions and oxidative processes are probably very similar for the PAH mixtures all through the year. The ratios of IP/(IP+BgP) are similar to those observed after fossil fuel combustion, while Phe/(Phe+Ant) and BaA/(BaA+Chr+Tri) are lower than ratios observed in source emissions (Rogge et al., 1993; Galarneau, 2008). The absence of clear source apportionment results for the ratios of Phe/(Phe+Ant) and BaA/(BaA+Chr+Tri) is probably caused by the semi-volatile character of these compounds resulting in larger partitioning in the gas phase and more exposure to oxidation processes, and thus lower isomer ratios. Indeno[123cd]pyrene and benzo[ghi]perylene are less volatile and completely in the particulate phase. This results in less oxidation and a better reflection of the possible emission source, which are fossil-fuelled traffic emissions in this case.

Table 7.3. Average and standard deviation (ng m^{-3}) of some carcinogenic PAH analysed during the sampling period in the quartz fibre filters.

	PM_{10} Particle phase ng/m^3		$PM_{2.5}$ Particle phase ng/m^3		PM_1 Particle phase ng/m^3	
Number of simples	20		8		8	
	Average	**S.D.**	**Average**	**S.D.**	**Average**	**S.D.**
Phenanthrene	0.056	0.025	0.046	0.010	0.039	0.011
Anthracene	0.006	0.003	0.004	0.001	0.003	0.001
Fluoranthene	0.136	0.076	0.105	0.044	0.084	0.046
Pyrene	0.186	0.112	0.143	0.064	0.115	0.057
Benz[a]anthracene	0.124	0.084	0.132	0.076	0.114	0.062
chrysene+triphenylene	0.265	0.174	0.268	0.151	0.218	0.131
Benzo[b+j]fluoranthene	0.129	0.091	0.194	0.095	0.173	0.089
Benzo[k]fluoranthene	0.096	0.068	0.125	0.069	0.107	0.068
benzo[e]pyrene	0.290	0.158	0.317	0.155	0.300	0.147
benzo[a]pyrene	0.143	0.125	0.191	0.146	0.178	0.135
indeno[123cd]pyrene	0.109	0.076	0.181	0.079	0.160	0.075
dibenz[a]anthracene	0.032	0.028	0.060	0.026	0.056	0.023
benzo[ghi]perylene	0.315	0.164	0.331	0.119	0.322	0.108
Total	1.887	1.182	2.096	1.034	1.869	0.954

7.2.2. Toxicological characterization

Figure 7.3 shows PSA dose-response curves of $PM_{2.5-10}$ and $PM_{0.1-2.5}$ samples and the corresponding logarithmic regression line, which allows the calculation of the TD_{50} values, and Table 7.4 provides TD_{50} average concentrations and standard deviation values for each of the atmospheric scenarios. Results indicate differences regarding chemical composition depending on the air masses, with a major capability of fine and coarse particles to cause oxidative DNA damage under stagnant conditions (28.2 and 128.6 μg ml^{-1}, respectively). Both sizes of particles show a lower reactivity during cleansing advection (146.8 μg ml^{-1} for coarse and 44.0 μg ml^{-1} for fine particles), although with high standard deviation values, which could be due to: (a) the effect of local emissions on chemical composition and/or (b) aggregation of particles in the aqua-phase resulting in differences in the toxicological behaviour of samples with similar properties.

A)

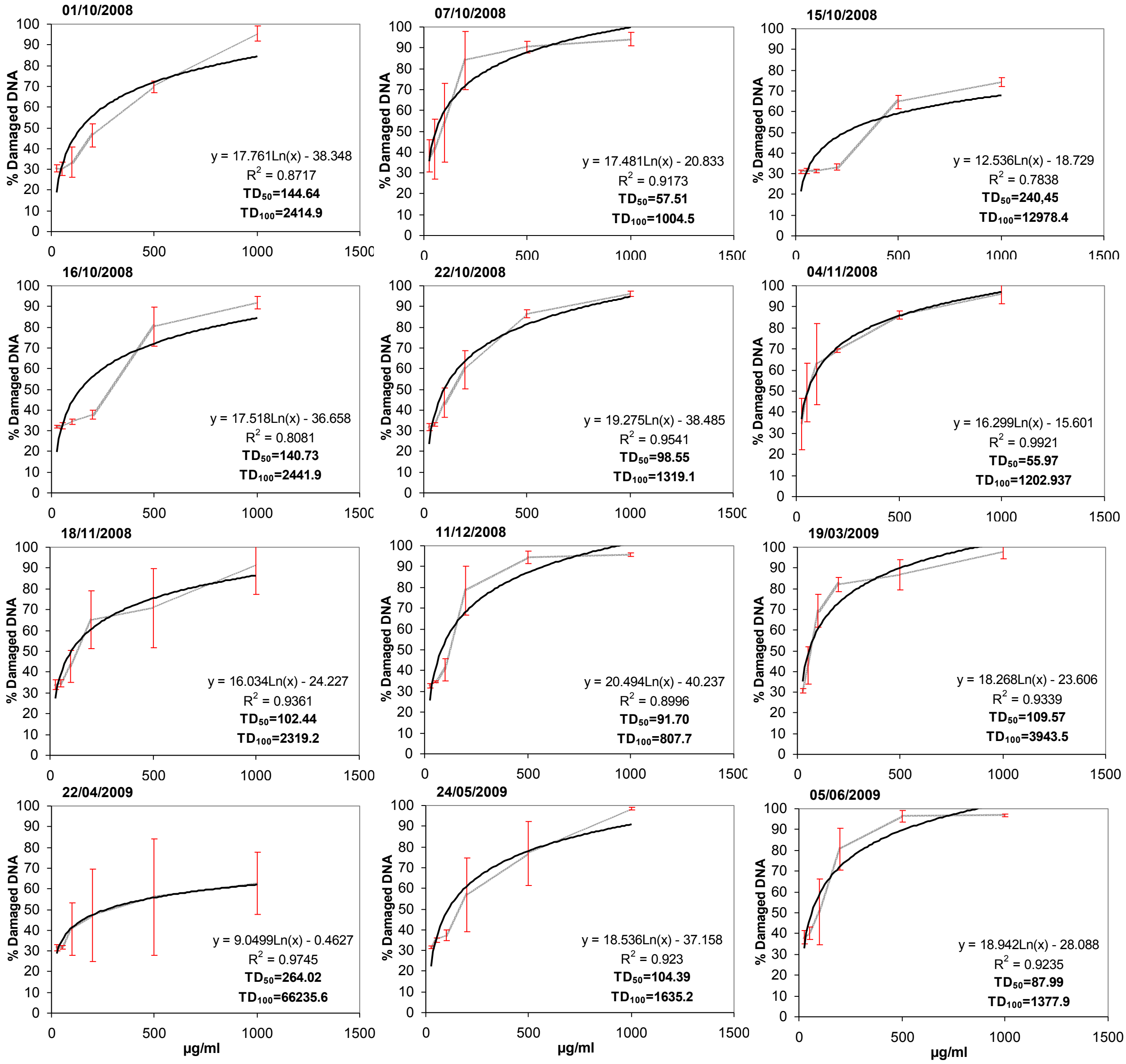

Figure 7.3. PSA dose-response curves of $PM_{2.5-10}$ (A) and $PM_{0.1-2.5}$ (B) samples from HVCI collections (mean ± standard deviation) and the corresponding logarithmic regression line. The dose (µg ml^{-1}) able to generate 50% and 100% of damage are indicated.

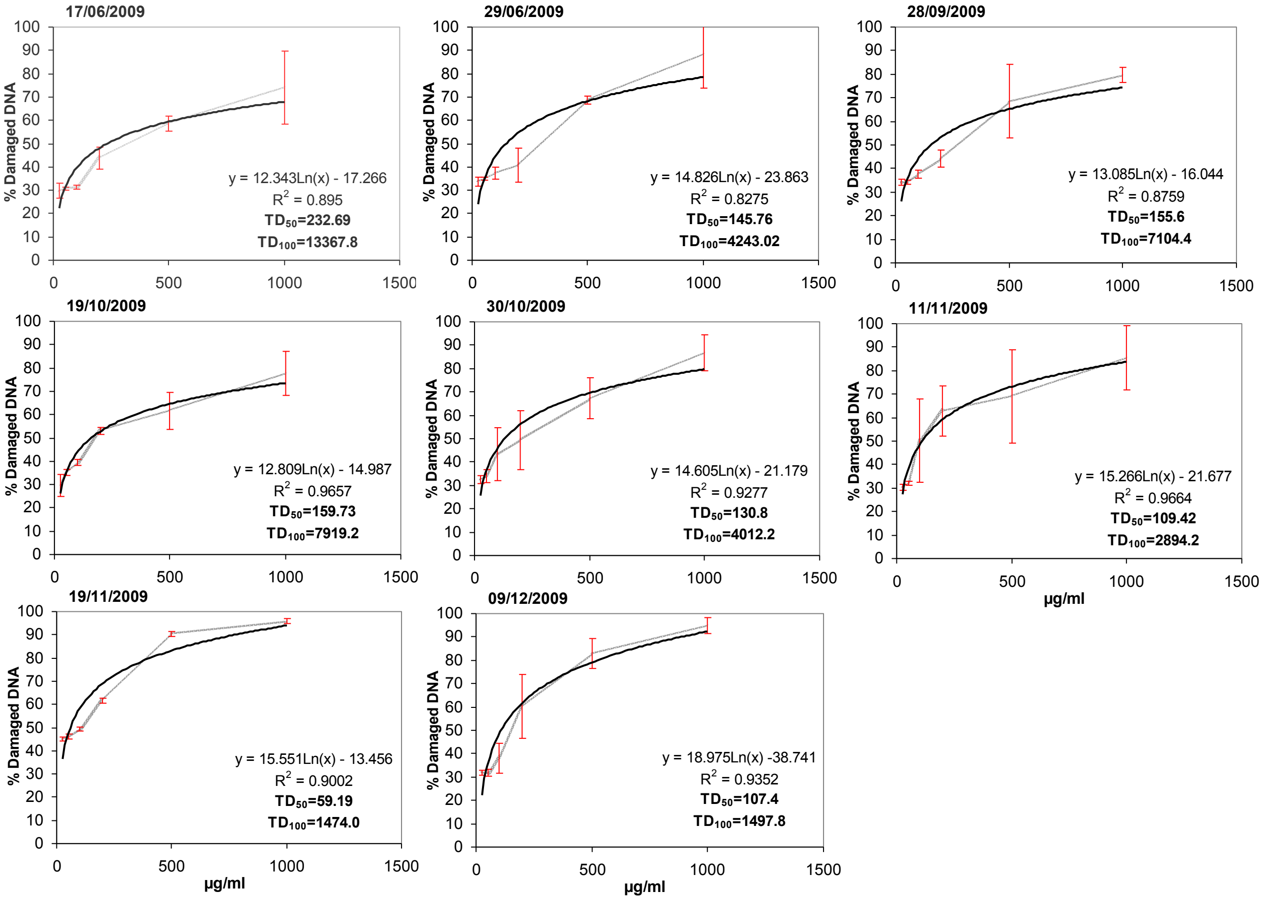

Figure 7.3. Continuation.

B)

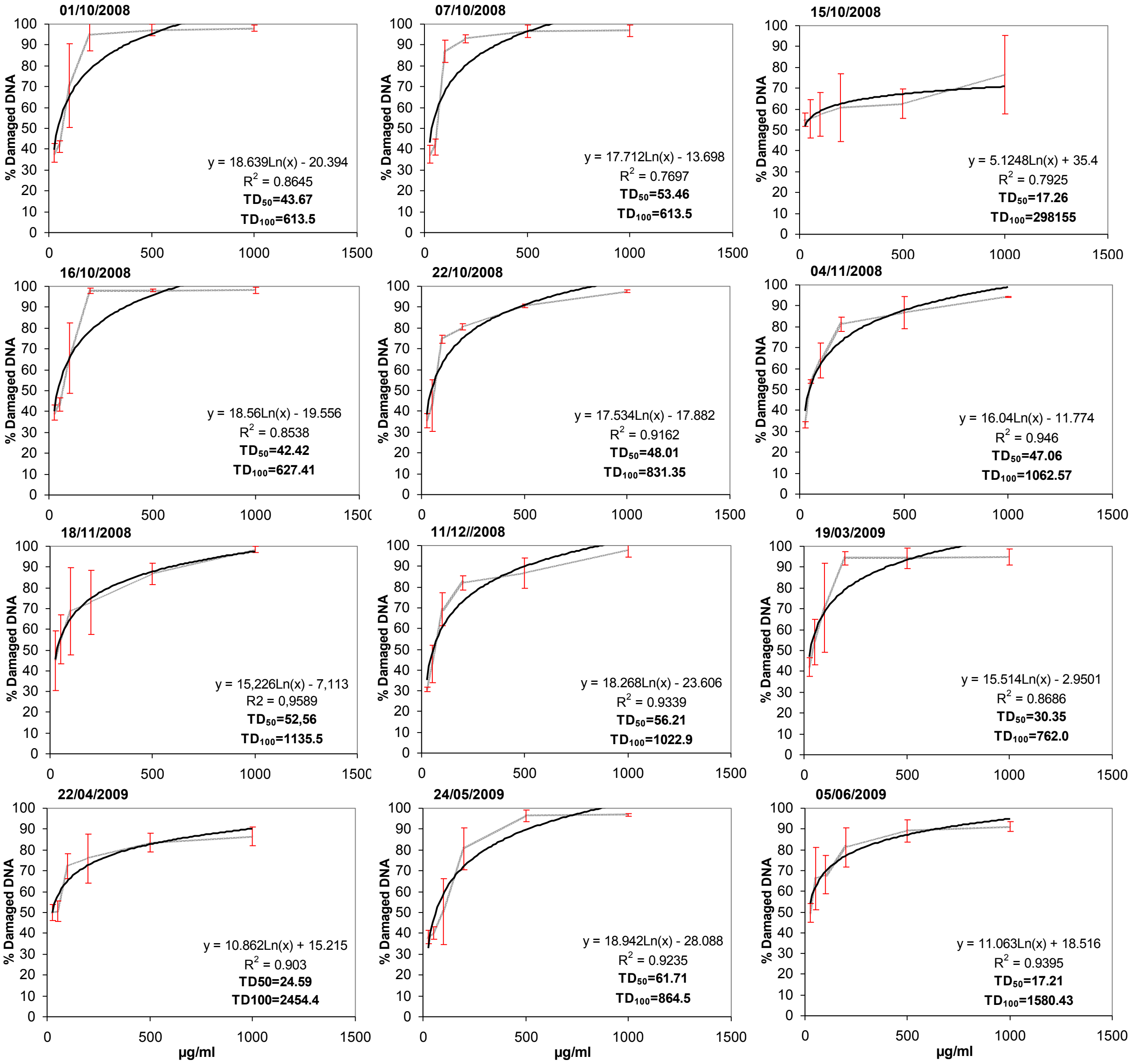

Figure 7.3. Continuation.

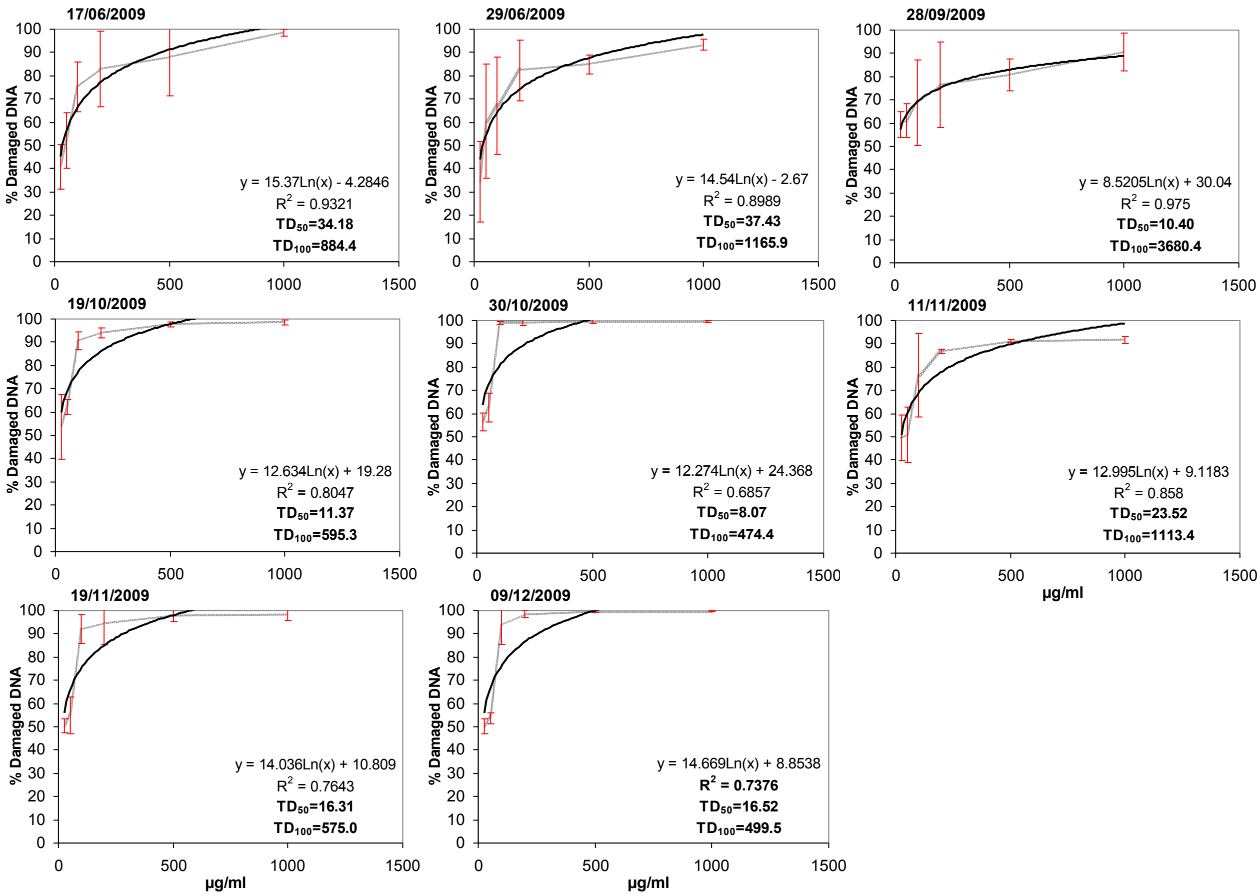

Figure 7.3. Continuation.

Table 7.4. TD_{50} average concentrations and standard deviation values expressed in $\mu g ml^{-1}$ for each of the different scenarios during the sampling period.

	TD_{50} ($\mu g\ ml^{-1}$)			
	$PM_{2.5-10}$		$PM_{0.1-2.5}$	
	Average concentration	St. Deviation	Average concentration	St. Deviation
AT	138.5	92.9	44.0	13.6
NAF	146.8	77.1	35.4	22.4
UP	128.6	44.4	28.2	16.2

Figure 7.4 shows TD_{50} concentrations for each day comparing the different grain sizes. TD_{50} average value for the coarse fraction in Barcelona (130 µg ml^{-1}; Table 7.5) is in the range of those reported in smoker houses in Beijing (Shao et al., 2007), during the smog episode occurring in London in 1950 (Whittaker et al., 2005), in industrial areas of Wales (Moreno et al., 2004) and in an urban background in Beijing during summer (Shao et al., 2006). Similarly, values for the fine fraction (32 µg ml^{-1}; Table 7.5) are

comparable to those obtained in Shanghai in autumn (Senlin et al., 2008), in a landfill area and an urban background site in Cardiff in winter 2000 (Greenwell et al., 2002), while Koshy et al. (2009) reported a much lower toxicity in this city during winter 2007 for the same fraction. Such seasonal variation in air pollution-induced Oxidative Stress has been described in several other works (Clarke et al., 1999; Huang et al., 2003), with most of them agreeing on a higher association of PM-reactivity with mortality for summer (Stieb et al., 2002; Goldberg et al., 2003). Our results in Barcelona show an oxidative capacity about 20% higher during autumn than during spring for both coarse and fine samples. Similar trends have been reported in previous studies (Senlin et al., 2008; Becker et al., 2005) and linked to an enhanced presence of soot aggregates (and therefore PAH and BC levels) and fly ash particles during autumn (Dachs and Eisenreich, 2000). A further explanation for the finest particles being more oxidative may be the higher levels of hazardous transition metals in autumn in this size fraction.

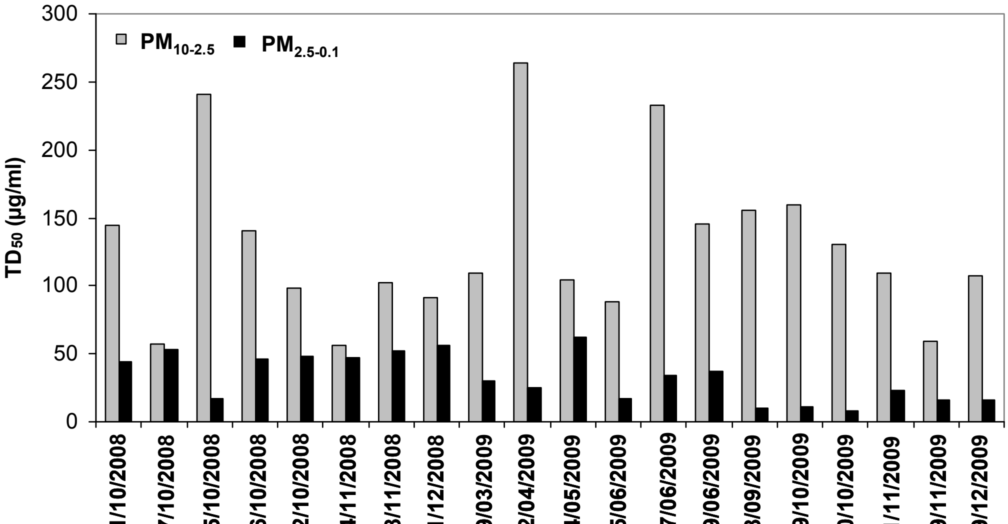

Figure 7.4. TD$_{50}$ values for PM$_{2.5-10}$ and PM$_{0.1-2.5}$ fractions.

Table 7.5. Average TD_{50} values from the DNA assay for different backgrounds

Study	Site	Background	Size	Date	TD_{50} (µg/ml)
Greenwell et al., 2002	Cardiff (UK)	Urban	$PM_{2.5-10}$	Winter 2000	13
			$PM_{2.5}$	Winter 2000	20
Moreno et al., 2004	Port Talbot (UK)	Urban-industrial	$PM_{2.5-10}$	Autumn 2002	151
Shao et al., 2007	Beijing (China)	Indoor	PM_{10}	July 2003	100
Whittaker et al., 2005	London (UK)	Urban	TSP	Winter 1952	150
Shao et al., 2006	Beijing (China)	Urban	PM_{10}	Summer 2002	116
Senlin et al., 2008	Shangai (China)	Urban	$PM_{2.5}$	Spring 2005	45
				Summmer 2005	51
				Autumn 2005	21
				Winter 2005-2006	9.4
Koshy et al., 2009	Cardiff (UK)	Urban	$PM_{0.1-2.5}$	2007	185
		Urban	$PM_{2.5-10}$	2007	493
		Urban-landfill	$PM_{0.1-2.5}$	2007	28
This study	Barcelona (Spain)	Urban	$PM_{2.5-10}$	2008-2009	130
		Urban	$PM_{0.1-2.5}$	2008- 2009	32

Associations obtained between the concentrations of specific transition metals in the $PM_{2.5-10}$ (PM_{10}-$PM_{2.5}$) or in the $PM_{2.5}$ fraction and the percentage of damaged DNA in the equivalent grain size were not significant. This could be due to the redox activity of PM-associated metals not being dependant only on their concentration but also on their bioavailability and oxidation state (Nawrot et al., 2009). Although organic chemicals are also expected to contribute significantly to the redox activity (Olivares et al., 2011), correlations between PAHs and TD_{50} values were not found since the extraction method with Mili-q water for the DNA assay is not able to effectively dissolve the PAHs and thus, the PSA analysis results could not show the toxicity of these compounds. Therefore, the main objective of the analysis of PAHs was to attain a correlation between the toxicity shown by the calculated toxicity equivalent of benzo[a]pyrene (BaPteq) and by the TD_{50} values in order to check if both methodologies provided similar information about the reactivity of the urban PM of Barcelona. The statistical analysis did not show an agreement between methodologies (r^2=0.2).

With regard to the DCFH results, a high correlation between the percentage of damaged DNA and equivalent H_2O_2 production for each sample (in four different concentrations) was observed (r^2= 0.62; Spearman's Rank Correlation (rs) = 0.83, $p < 0.05$; this statistical analysis was provided in Minitab 15 (Microsoft Inc, WA, USA; Noether et al., 1991. Thus, the use of the oxidant-sensitive probe DCFH in this study suggested the moderate positive association between the amount of DNA damage and the generation of reactive species, as has noted in previous studies (Koshy et al., 2009).

7.2.3. Source apportionment and human health risk estimate

The analysis of the chemical data allowed selecting 43 species (Al, Ca, Fe, K, Mg, Na, S, Mn, Ti, Li, V, Cr, Co, Ni, Cu, Zn, As, Rb, Sr, Cd, Sn, Sb, La, Pb, Ba, OC, EC, NO_3^-, Cl^-, NH_4^+, phenanthrene, anathranece, fluoranthene, pyrene, benzo[a]anthracene, chrysene+thriphenylene, benzo[b+j]fluoranthene, benzo[k]fluoranthene, benzo[e]pyrene, benzo[a]pyrene, indeno[123cd]pyrene, dibenzo[a]anthracene, benzo[ghi]perylene) out of 76 to perform the source apportionment study for a total of 392 samples. The ME-2 model provided robust results for an 8-sources solution with the constraints described in the methodology section. The r^2 value between the observed and predicted mass concentration was 0.9. The Q-main values for the base and continuation runs were 18378 and 20324 respectively (13760 degrees of freedom), revealing an acceptable increase of 10% due to the constraints introduced to the basic PMF model.

The eight identified factors were vehicle exhaust (23% $PM_{2.5}$), secondary nitrate/organics (10% $PM_{2.5}$), secondary sulphate/organics (13% $PM_{2.5}$), mineral matter (19% $PM_{2.5}$), sea salt (3% $PM_{2.5}$), fuel oil combustion (14% $PM_{2.5}$), industrial processes (10% $PM_{2.5}$) and road dust (8% $PM_{2.5}$), identified by means of the methodology developed by Amato et al. (2009a). Vehicle exhaust particles represent the emissions from vehicle engines, excluding secondary inorganic species. It explains the 60% of the total variation of OC and the 70% of the EC. This factor also includes the 20-45% of all the considered PAHs, being the major contributor of the particle-phase of these compounds, followed by industry (25% on average) and fuel-oil combustion emissions (7% on average). The occurrence of K in this factor may also reveal a small contribution from biomass burning. The secondary nitrate/organics factor is mainly composed by NO_3^- and NH_4^+. The third factor, traced by S and NH_4^+, is the result of the formation of secondary sulphate in atmosphere from the photochemical oxidation of sulphur oxides initially emitted as gases from local emissions (utilities and power plants) and from long range transport. The mineral factor accounts for several sources of mineral matter, excluding resuspension by traffic. Therefore, this factor is identified as the resuspension from urban working areas, gardens and unpaved parking areas. It explains the 55% of the total variation of Al and Ca. It is important to note that the contribution of this source to PM levels is much higher than in previous studies (Pérez et al., 2008; Amato et al., 2009a), probably as a result of the intensive construction-works close to the sampling site during 2008, if excluding this year from the analysis this contribution decrease to 26% in PM_{10}, more close to historic results in the city. The sea salt factor represents the 70% of the total variation of Na, the 50% of Cl^- and also the 30% of NO_3^- . Fuel oil combustion is characterized by high concentrations of S, V and Ni reflecting the influence of industrial combustion processes and ship emissions. The industrial component presents high concentrations of Pb, Zn, Fe, Mn, Cd and PAHs and was related to the mixed influence of industrial activities located in the area such as smelters and cement kilns. Finally, the last factor, considerably enriched in Fe, Cu and Sb, was attributed to road dust.

As mentioned in the methodology section, the cancer risk from exposure to each obtained source was calculated as the sum of risks of all available species in their sources following the methodology of Wu et al. (2009) and considering only those metals and PAHs which have known toxicity values according to the Integrated Risk Information System, the California Environmetal Protection Agency and the USEPA Regional Screening Level. This includes As, Cd, Co, Cr, Ni, Pb, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, benzo[b+j]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[123cd]pyrene, diben[a]anthracene and benzo[ghi]perylene. Thus, the mean source specific concentrations of atmospheric pollutants with an associated cancer unit risk are shown in Table 7.6, where the estimation of excessive cancer risk for the identified factors is summarized. These results were obtained using the available unit risks for As ($4.3x10^{-3}$ risk/μgm^{-3}), Cd ($4.2x10^{-3}$ risk/μgm^{-3}), Co ($9.0x10^{-3}$ risk/μgm^{-3}), Cr ($2.4x10^{-3}$ risk/μgm^{-3}), Ni ($4.8x10^{-4}$ risk/μgm^{-3}), Pb ($1.2x10^{-5}$ risk/μgm^{-3}), fluorene ($1.1x10^{-6}$ risk/μgm^{-3}), phenanthrene ($1.1x10^{-6}$ risk/μgm^{-3}), anthracene ($1.1x10^{-5}$ risk/μgm^{-3}), fluoranthene ($1.1x10^{-6}$ risk/μgm^{-3}), pyrene ($1.1x10^{-6}$ risk/μgm^{-3}), benz[a]anthracene ($1.1x10^{-4}$ risk/μgm^{-3}), benzo[b+j]fluoranthene ($1.1x10^{-4}$ risk/μgm^{-3}), benzo[k]fluoranthene ($1.1x10^{-4}$ risk/μgm^{-3}), benzo[a]pyrene ($1.1x10^{-3}$ risk/μgm^{-3}), indeno[123cd]pyrene ($1.1x10^{-4}$ risk/μgm^{-3}), diben[a]anthracene ($1.1x10^{-3}$ risk/μgm^{-3}) and benzo[ghi]perylene ($1.1x10^{-5}$ risk/μgm^{-3}). For the PM_{10} fraction all sources except the two secondary aerosols factors and vehicle exhaust gave a sum of cancer risks higher than the acceptable level of $1x10^{-6}$, according to the EPA Cancer Risk Guidelines, while in the case of $PM_{2.5}$, also sea salt gave a lower level than the acceptable one. For the PM_1 mass fraction, only fuel oil and industrial emissions gave a significant risk. The lower risk of carcinogenesis showed by the exhaust emissions in spite of the several metals and PAHs associated with this source is due to the lack of consideration of volatile organic compounds (VOCs), which have been reported to be the main responsible of cancer risk of gasoline and diesel vehicles in previous studies (Wu et al., 2009), these compounds are mainly related to the traffic emissions in the urban background environment of Barcelona, this association could be confirmed from the data set obtained during the DAURE campaign (Figure 7.5). However, it is important to note that considering traffic as the sum of road dust, exhaust emissions and the 70% of secondary nitrate, the risk associated with this source is the major one in the PM_{10} fraction and exceeded only by the industrial factor in the $PM_{2.5}$ and by the industrial and the fuel oil factors in the PM_1. The secondary is the approximate share of secondary nitrate/organics due to mobile sources in Barcelona. It has been already reported in previous studies (Ostro et al., 2011). The sum of cancer risks were 2.0 10^{-5}, 1.1 10^{-5} and 5.5 10^{-6} for PM_{10}, $PM_{2.5}$ and PM_1 fractions, respectively, decreasing with mass concentration. It is important to take into account that risks are multiplied by mass and that the surface area of particles is not consider in this estimate (Mukerjee and Biswas, 1992; Wu et al., 2009). Thus, final cancer risks for PM_1 are lower than for PM_{10}. The overall risk value for the PM_{10} fraction in this work is lower than those obtained in previous studies (Los Angeles, USA: $1.0x10^{-4}$; New York City, USA: $1.3x10^{-4}$; Sax et al., 2006), as these works considered VOCs in the analysis. On the other hand, the risk value for the $PM_{2.5}$ fraction is in the range of that reported by Wu et al. (2009) (Seattle, USA: $1.2x10^{-5}$), although they also included VOCs in their risk estimation. This fact could be interpreted as reflecting a higher toxicity of chemical composition of $PM_{2.5}$ in Barcelona.

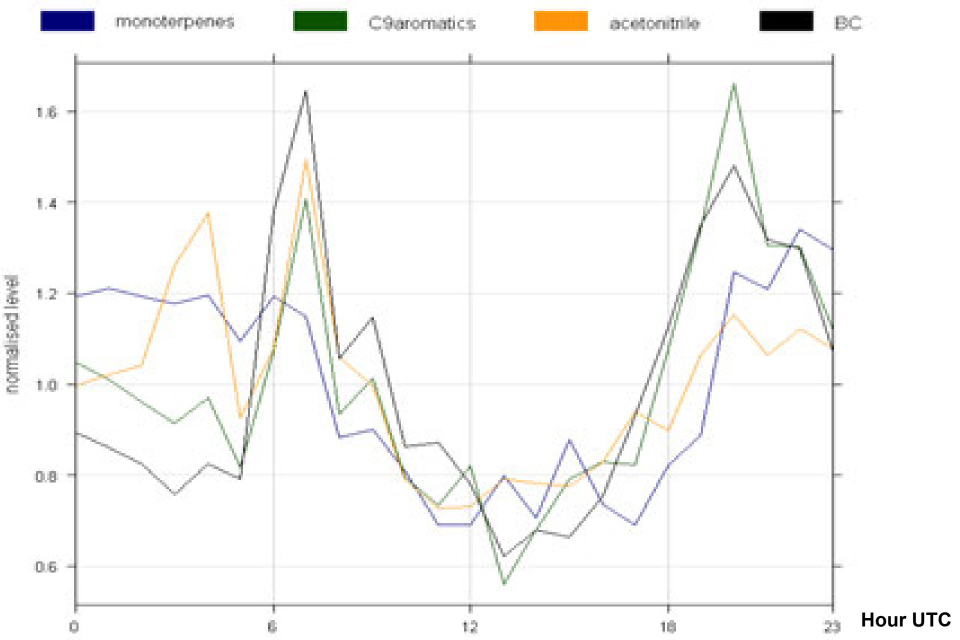

Figure 7.5. Time variation of monoterpenes, acetonitrile, C9 aromatics and BC measured during the DAURE campaign.

Table 7.6. Estimates of the cancer risk for each source by the risk apportionment approach.

	Sea Salt	Fuel oil	Industrial	Road dust	Secondary Nitrate	Exhaust	Secondary sulphate	Mineral
PM_{10}-RISK*								
Trace metals	1.2E-06	2.6E-06	2.8E-06	6.0E-06	6.2E-07	6.9E-07	6.4E-07	5.2E-06
PAHs	0.0E+00	0.0E+00	4.0E-08	0.0E+00	0.0E+00	9.0E-08	0.0E+00	0.0E+00
Sum risk	1.2E-06	2.6E-06	2.9E-06	6.0E-06	6.2E-07	7.8E-07	6.4E-07	5.2E-06
$PM_{2.5}$-RISK*								
Trace metals	2.9E-07	2.0E-06	2.7E-06	1.7E-06	5.3E-07	6.7E-07	7.7E-07	1.8E-06
PAHs	0.0E+00	0.0E+00	3.8E-08	0.0E+00	0.0E+00	8.7E-08	0.0E+00	0.0E+00
Sum risk	2.9E-07	2.0E-06	2.8E-06	1.7E-06	5.3E-07	7.5E-07	7.7E-07	1.8E-06
PM_1-RISK*								
Trace metals	2.5E-08	1.5E-06	1.8E-06	4.1E-07	3.0E-07	5.9E-07	6.7E-07	1.5E-07
PAHs	0.0E+00	0.0E+00	2.5E-08	0.0E+00	0.0E+00	7.7E-08	0.0E+00	0.0E+00
Sum risk	2.5E-08	1.5E-06	1.8E-06	4.1E-07	3.0E-07	6.7E-07	6.7E-07	1.5E-07

Figure 7.6 shows the mass and the risk estimate contributions of each source to PM_{10}, $PM_{2.5}$ and PM_1 fractions. Mineral matter and road dust were the primary risk sources in the PM_{10} fraction, while mineral matter, road dust, industry and fuel oil combustion were the main sources in the $PM_{2.5}$ fraction and industry and fuel oil combustion in the PM_1. The high contribution of mineral dust sources during the days under study is clearly influencing the cancer risk estimation presented here, so further studies are needed in order to confirm the urban background risk assessment. Fuel oil

combustion and industry emissions show the higher differences in contribution when considering mass or risk estimates, this being in agreement with previous studies reporting a substantially higher genotoxic risk of these sources than mostly traffic-related emissions when considering particulate phase compounds (Topinka et al., 2011).

As DNA oxidative damage has been associated with cancer initiation in several studies (Møller et al., 2008), the sum cancer risk for each of the selected days for ROS-generating analysis was calculated for the $PM_{2.5-10}$ (PM_{10}-$PM_{2.5}$) and the $PM_{2.5}$ fractions in an attempt to find associations with TD_{50} values (Figure 7.7). A high correlation has been obtained for the fine fraction ($r^2=0.83$), although one should be cautious concluding a direct relation as only eight simultaneous days were available for the $PM_{2.5}$ fraction. This high association between methodologies for health impact estimation highlights a relationship between PM-induced DNA damage and the initiation of carcinogenesis. However, it is important to highlight that DNA damage does not necessarily lead to cancer development, due to the DNA repairing mechanisms, which capacity was not known in this case. No correlation was obtained for the coarse fraction ($r^2=0.21$). The bioreactivity pattern of these samples is very different from those registered for the fine fraction as composition is dominated by mineral and sea salt, which have been reported to generate less DNA damage (Nawrot et al., 2009). Comparisons between methodologies are subject to many uncertainties given that they have been carried out with different samples collected on different materials and with different cutting sizes. These factors can cause differences on the chemical composition, which probably reflects on the health risk estimation. Indeed, the cancer risk assessment of the $PM_{2.5-10}$ fraction has been estimated from that obtained for the PM_{10} and the $PM_{2.5}$ fractions, which add a certain uncertainty to the comparison.

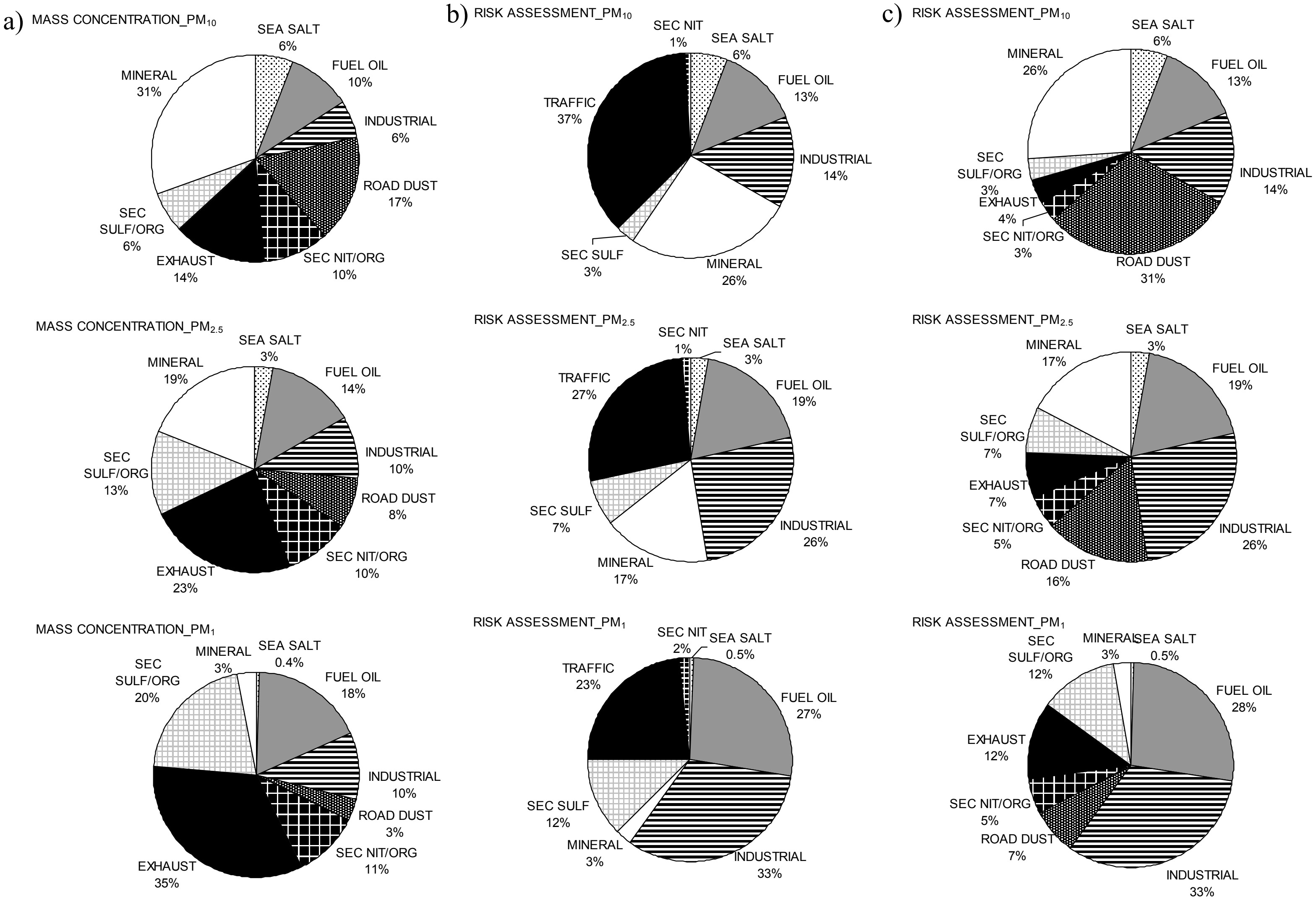

Figure 7.6. Source contributions to PM_{10}, $PM_{2.5}$ and PM_1 for January 2008 to December 2009: (a) mass contributions, (b) risk estimates contributions, (c) risk estimates contributions with traffic disaggregate into factors (road dust, exhaust and 70% of the secondary nitrate).

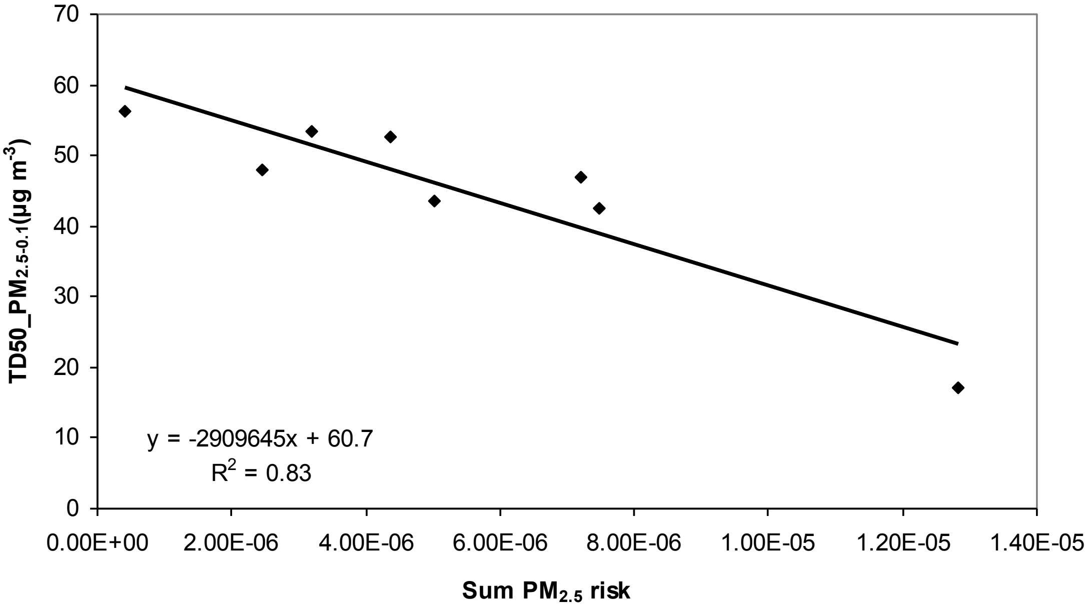

Figure 7.7. TD_{50} values vs. Sum Risk estimates in the $PM_{2.5}$ fraction for the selected days.

7.3. CONCLUSIONS

The average TD_{50} values for the studied period show $PM_{0.1\text{-}2.5}$ samples (32 µg ml^{-1}) to be more toxic than the $PM_{2.5\text{-}10}$ fraction (130 µg ml^{-1}). This indicator of toxicity did not appear to be strongly dependent on the three different meteorological scenarios (NAF, UP, AT). TD_{50} values reported in Barcelona were in the range of previous studies in highly polluted urban areas.

Associations obtained between the concentration of a specific transition metal or the sum of all metals and the percentage of damaged DNA were not significant; this perhaps being due to the fact that the redox activity of PM-associated metals depends not only on their concentration but also on their bioavailability and oxidation state (Nawrot et al., 2009). These findings seem to indicate that the main controlling factor of the aerosols toxicity in the city of Barcelona is particle size, probably related with the available surface area of the particles, which has been defined as the most important determinant of effect for fine and utrafine particles (Risom et al., 2005). Further studies are needed in order to elucidate which is the role of the chemical composition.

The use of the oxidant-sensitive probe DCFH in this study and the correlation with the PSA test results, confirmed the positive association between the amount of DNA damage and the generation of reactive species.

The chemical composition of particles during 2008 and 2009 allowed us to obtain the main air pollution sources in the city and so estimate their cancer risk contributions to that of total PM. Fuel oil combustion and industrial emissions appear to provide the largest contribution to risk, although it is important to note that considering traffic as the sum of exhaust emissions, road dust and the 70% of secondary nitrate, this source accounts for the major toxicity in the PM_{10} fraction. The sum of cancer risk estimates calculated for each of the selected days for toxicological characterization was found to correlate with TD_{50} values in the fine fraction although no correlations were found in the coarse fraction. Overall, our study of ambient PM bioreactivity in Barcelona illustrates that there is a great chemical complexity and that the resulting uncertainties can be reduced by combining different methodologies in order to obtain a clearer picture of the impact of ambient PM on the generation of human diseases.

ACKNOWLEDGEMENTS

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ADDITIONAL FINDINGS

On-line characterization of exposure risk: Lung-deposited surface area

A7.1. INTRODUCTION

The enhanced toxicity of atmospheric particles appears to be associated with surface chemistry and the larger specific surface area that ultrafine particles have (Oberdörster et al., 2005; Stoeger et al., 2006). In view of the prevalence of nanoparticle aggregates in urban air, it is important to assess the surface area and volume doses of these particles when they are inhaled. Tran et al. (2005) showed that the level of inflammation by different particle dusts in the lungs of rats could be better explained when the lung burden was expressed as total particle surface area instead of PM mass. Elder et al. (2005) found that particle surface area is an important parameter affecting inflammatory and histopathological effects of inhaled particles on the lung tissue of rats. Oberdörster (2000) suggested that aerosol surface chemistry appears to play an important role in ultrafine particle toxicity, more than any other mechanistic pathway for interaction of particles with lung cells. In addition, Stoeger et al. (2006) demonstrated that the PM surface area was best correlated with lung cell inflammation in mice when exposed to six different vehicle exhaust-like aerosols, and that the correlation was even more high than with particle organic carbon content at the same mass dosage. In a study on children school in Austria, the particle surface concentration measured with a diffusion charger has been associated with lung function and pulmonary symptoms (Moshammer and Neuberger 2003); and in Atlanta, the geometric surface area of particles in the 10-100nm diameter range has been associated with acute respiratory visits to an ambulatory medical facility (Sinclair and Tolsma 2004). In sum, all these studies indicate that the surface concentration of ambient particles in different environments is a very useful parameter in the efforts to associate health effects with exposure to PM.

However, relatively few techniques are available to monitor exposures with respect to aerosol surface area; including the BET method, the photoelectric aerosol sensor (PAS), the epiphaniometer and different models of diffusion chargers. The BET measurement (Brunauer, Emmett and Teller, 1938), based on a gas adsorption method, is not suited for a rapid evaluation of aerosol surface area at lower concentrations and it can be only used for powders, not for particles in the gasborne state. In addition, the BET measures the total surface, as opposed to the available surface (Fuchs surface) measured by other techniques, which is better related to health effects. In the epiphaniometer (Baltensperger et al., 1988), radioactive lead atoms attach to particles by diffusion. The particles are then collected on a filter and the “Fuchs” surface area is determined by measuring the α–activity of the attached atoms. The “Fuchs” surface corresponds to the epiphaniometer signal and is directly proportional to the particle surface area that is available for diffusion. This instrument is not well suited to widespread use in workplaces or Air Quality networks because of the inclusion of a radioactive source and toxic lead, and the lack of effective temporal resolution. The PAS (Matter et al., 1999) consists on irradiating particles with ultraviolet light in order to emit photoelectrons from the particle surface, which then becomes positively charged. The particle charged is determined by an electrometer after particle collection on a filter. PAS response largely depends on the surface chemistry and it is mainly used for qualitative characterization of aerosol concentrations. One of other possible methods is diffusion charging (DC) which measures the surface area indirectly (Hinds et al., 1999). When nanoparticles are exposed to an unipolar ion environment, they acquire a charge level which, at least in a certain particle size range, is theoretically proportional to the particle surface area (Rogak et al., 1993).

Several studies have confirmed that diffusion chargers have a strong potential to be used alone as particle surface monitors or in combination with other instruments to provide information on particle properties, such as the mean surface diameter (combined with a CPC) or qualitative surface chemistry characteristics (in combination with a PAS), in real time (Woo et al., 2001; Ntziachristos et al., 2004; Bukowiecki et al., 2002; Mohr et al., 2005; Ntziachristos et al., 2007).

Given the potential role of the available surface area on the aerosol toxicity, the time variation of the lung deposited surface area in the alveolar region was studied simoultaneously with other on-line measurements (PM, Black Carbon, particle number and gaseous pollutants) to elucidate which factors and sources govern this parameter. To that end, a diffusion charger (NSAM 3550, TSI) was deployed in an urban background site in the city of Barcelona from November 2011 to February 2012.

A7.2. RESULTS AND DISCUSSION

A7.2.1. LDSA levels and comparison with previous studies

Figure A7.1 shows the time series of the lung deposited surface area (LDSA), N, BC and PM_{10} values for the whole sampling campaign. The meteorological scenarios during the measurements included the alternance of periods governed by regional recirculation of air masses and subsequent accumulation of pollutants at local levels, Atlantic advection episodes cleansing the atmosphere, and a short period accounting for the arrival of European air masses, which typically result in an increase of the PM levels (Pey, 2007). All parameters show a clear dependency on this alternance, with maximum levels during the accumulation days (Table A7.1), with the exception of PM_{10}, $PM_{2.5}$ and PM_1 with very similar levels to those registered during the European episode. Mean levels of BC, LDSA and PM_X decreased by 30% on average during the Atlantic advection scenarios, while N decreased by 15%.

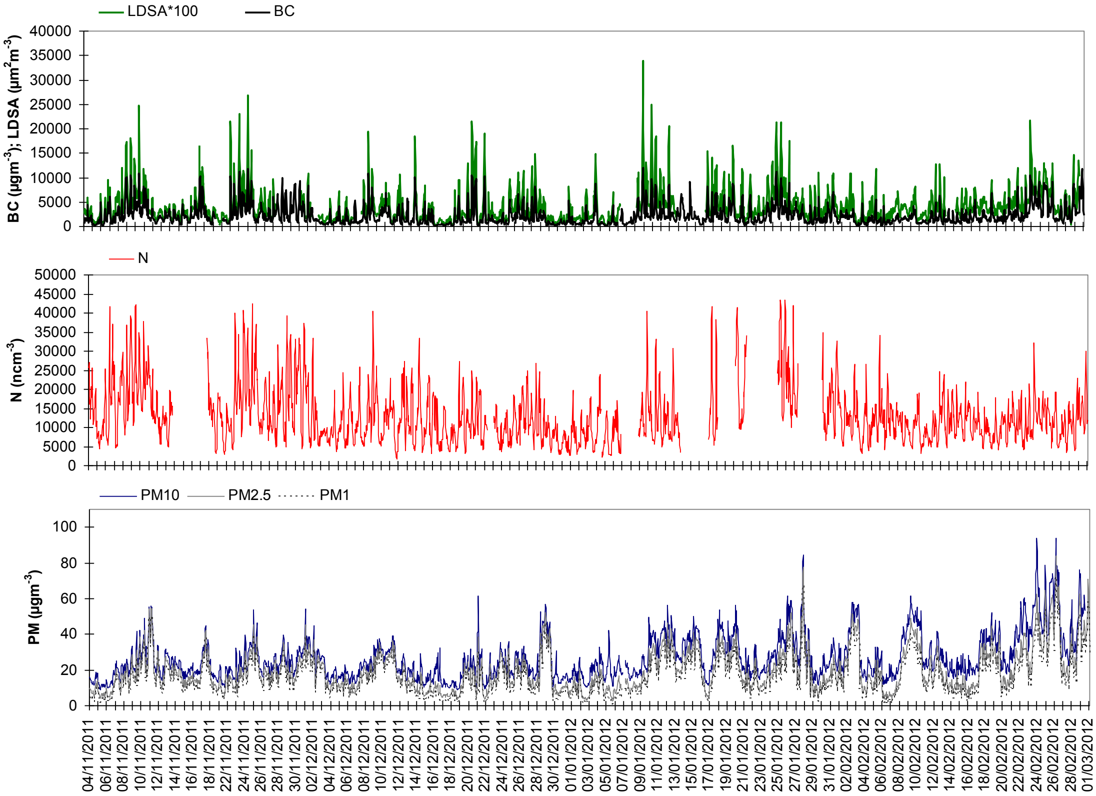

Figure A7.1. Time series of LDSA, BC and N during the whole measurement period.

Table A7.1. Mean, maximum and minimum concentrations and standard deviation values of a) LDSA, BC and N and b) PM_{10}, $PM_{2.5}$ and PM_1 for the different meteorological scenarios.

a)

	REGIONAL RECIRCULATION			ATLANTIC ADVECTION			EUROPEAN AIR MASSES		
	LDSA ($\mu m^2 m^{-3}$)	BC ($ng m^{-3}$)	N (ncm^{-3})	LDSA ($\mu m^2 m^{-3}$)	BC ($ng m^{-3}$)	N (ncm^{-3})	LDSA ($\mu m^2 m^{-3}$)	BC ($ng m^{-3}$)	N (ncm^{-3})
Mean	46.0	2446.6	13645.0	32.5	1738.0	11501.6	33.1	1419.1	11080.6
Max	339.0	12011.1	43533.8	215.1	10816.5	40365.9	127.8	6251.5	34171.1
Min	1.3	121.3	2276.6	1.2	111.0	1795.9	1.6	182.3	3062.5
St. Dev	35.5	2052.7	7908.2	32.6	1866.4	5889.9	21.9	980.2	5004.7

Table A7.1. Continuation.

b)

	REGIONAL RECIRCULATION			ATLANTIC ADVECTION			EUROPEAN AIR MASSES		
	PM_{10} (µgm^{-3})	$PM_{2.5}$ (µgm^{-3})	PM_1 (µgm^{-3})	PM_{10} (µgm^{-3})	$PM_{2.5}$ (µgm^{-3})	PM_1 (µgm^{-3})	PM_{10} (µgm^{-3})	$PM_{2.5}$ (µgm^{-3})	PM_1 (µgm^{-3})
Mean	28.1	20.9	16.1	19.9	14.7	11.8	28.9	20.0	15.0
Max	100.6	93.6	70.0	61.4	54.6	50.0	65.2	56.0	42.7
Min	8.1	0.5	0.7	9.1	4.0	1.9	10.0	1.5	1.2
St. Dev	13.7	13.0	10.2	7.3	7.6	7.3	14.2	14.2	10.6

Table A7.2 summarizes LDSA results reported for different backgrounds in previous studies. Studies on this parameter have mainly focused on different indoor work environments, and it is not easy to find studies which could be compared with the results obtained in the urban background of Barcelona in order to obtain information about the state of the city. Thus, regarding only available outdoor studies, values are similar to those obtained in traffic sites in Zurich (Switzerland) and in urban background sites in Los Angeles (USA) and higher than in urban background sites in Zurich. At urban background sites located in cities with relatively low traffic emissions, PM size distribution is dominated by the accumulation mode, resulting in a lower surface area of particles than in cities with a higher density of vehicles. Values are much lower than in the reported work environments.

Table A7.2. LDSA results summarized by study.

Background	**Lung deposited surface area (µm^{2}cm^{-3})**			**Study**
	Total	**Alveolar**	**Tracheobronchial**	
Traffic-related ocuppational groups (bus drivers, bus mechanics) (Minnesota)	17-878			Ramachandran et al., 2005
Urban background site (Los Angeles)_Retirement Community (Indoor)		45		Ntziachristos et al., 2007
Urban background site (Los Angeles)_Retirement Community (Outdoor)		69		
Urban background site (Los Angeles)		53		
Traffic site (Los Angeles)		106		
Traffic site (Los Angeles)		153		
Indoor-Smoking session (Munich)		1E+08		Fromme et al., 2009
Indoor-Engine plant (Indeanapolis)	500			Heitbrink et al., 2009
Indoor-Restaurants (central Italy)		4E+02	63	Buonanno et al., 2010
Indoor-Automotive plants		700±340		Buonanno et al., 2011
Biogas Cookstove (India)		200±60		Sahu et al., 2011
Coal Cookstove (India)		65±20		
LPG Cookstove (India)		175±55		
Kerosene Cookstove (India)		700±300		
Highway (Zurich)		40		Fierz et al., 2011
Busy city road-1 (Zurich)		63		
Busy city road-2 (Zurich)		63		
Urban background site, inner city, little traffic (Zurich)		19		
Average city road (Zurich)		28		
Urban background site, no traffic (Zurich)		11		
Urban background with traffic influence (Barcelona)		42±37	9±10	This study

A7.2.2. Time variation and correlation between parameters

Figure A7.2 shows the daily cycle of LDSA, BC, N, PM_{10}, $PM_{2.5}$ and PM_1. The relation between the cycles of BC and LDSA (r^2=0.90) points at traffic as the main responsible for LDSA time variation, showing peaks at traffic rush-hours. These peaks would be related to the fresh exhaust emissions from traffic, characterised by small particle sizes and consequently large particle surface concentrations. When each day of study is investigated separately, it could be observed that for some days the time variation of LDSA levels seemed to better correlate with that of N during the central hours of the day (r^2= 0.96); two exemples are found in Figure A7.3), accounting also for high levels of PM_X during these hours. These days were characterized by wind speeds higher than 3.5m/s at midday. As described in chapter 4, midday N peaks may be linked to new particle formation processes by photochemistry, which could result in increased LDSA concentrations. Given that this monitoring campaign took place in winter, this phenomenon is not detected as frequently as it would be in summer.

The potential sources affecting the LDSA in the site under study were investigated by means of polar plots reported for the daytime and the night (Figure A7.4). At night the maximum LDSA concentrations are obtained for the lowest wind speeds, as observed for the BC levels, probably reflecting atmospheric stagnation and a reduction of the height of the boundary layer. As discussed above, during daytime, sources other than traffic are influencing the levels of LDSA and the wind-response of this parameter is more similar to that of N and PM_x levels, with high concentrations registered when the wind velocity is intense and the wind direction transport air masses from the south of the city, this pattern correspond with the breeze circulation. While the increase of N when maximum wind speeds have been associated to the secondary formation of particles, enhanced by the dilution of traffic-related pollutants, the higher solar radiation and the transport of gaseous precursors from the city, the low decrease of the PM_{10} concentrations at midday is associated with transport of pollutants from the city by breeze. In-depth investigation is needed to conclude which factors are the major responsible for the relatively high levels of LDSA associated with breeze circulation.

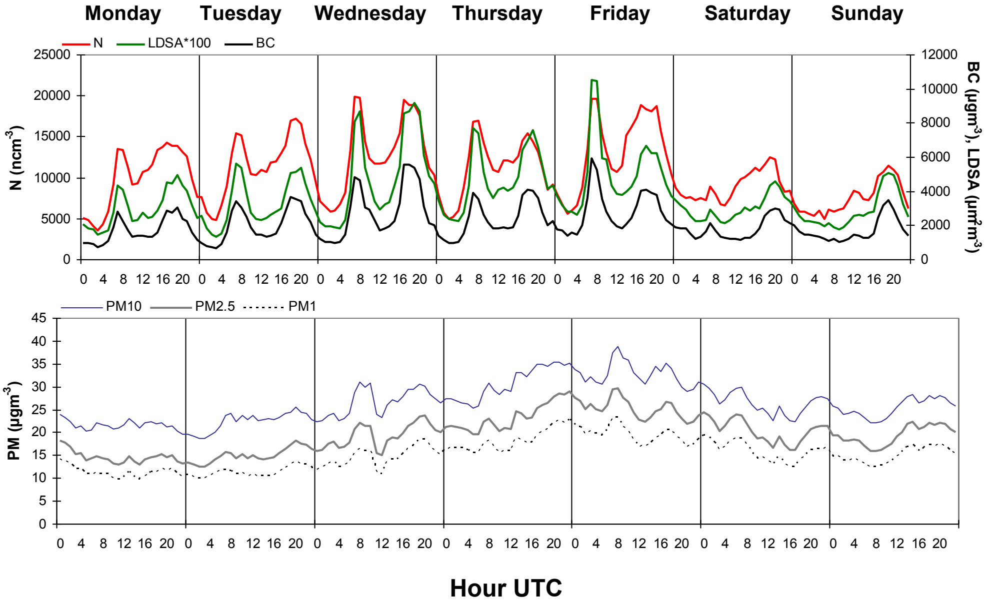

Figure A7.2. Daily cycles of LDSA, BC, N and PM_{10} in Barcelona.

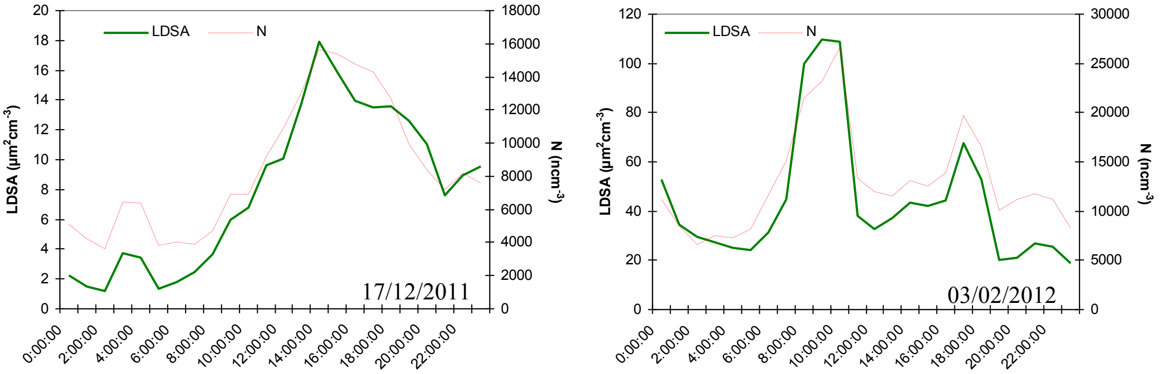

Figure A7.3. Two days with a high correlation coefficient between LDSA and N.

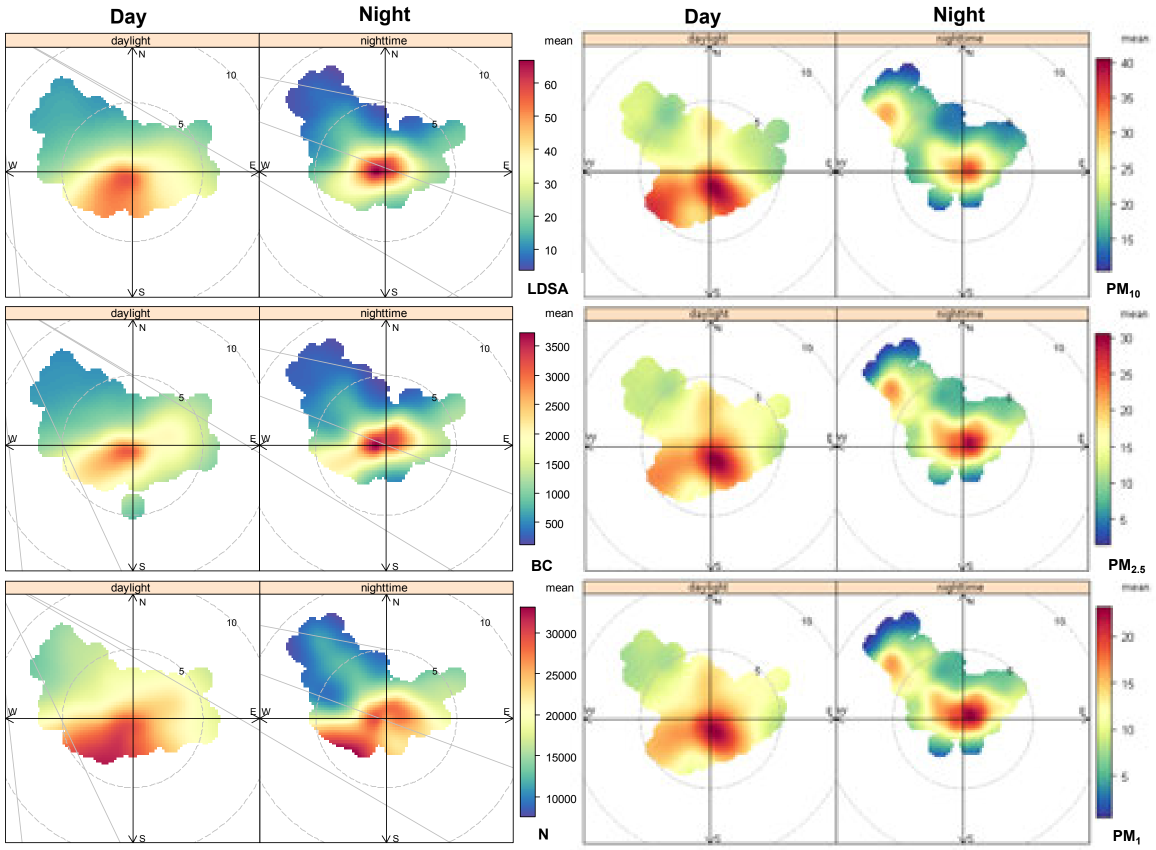

Figure A7.4. Polar plots of LDSA, BC, N, PM_{10}, $PM_{2.5}$ and PM_1 distinguishing the day and the nigth periods.

Figure A7.5 shows the correlation plots between LDSA and BC, N, PM_{10}, $PM_{2.5}$ and PM_1 as a function of the period of the day. Four different periods are distinguished: 7-9, 11-14, 18-21 and 1-3 UTC. The morning period stands for the traffic rush-hours, when the highest exhaust emissions are registered. 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 development of breezes, resulting 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. The night period is characterized by the lowest traffic intensity; but the decrease of the height of the mixing layer causes a concentration of pollutants. A high correlation coefficient between LDSA and BC was observed for all periods of the day, although lower r^2 were obtained at midday. It confirms traffic as the main responsible for LDSA levels in Barcelona, which is in accordance with the large surface area of particulate vehicle emissions.

During the morning and evening rush-hour, LDSA and N were mostly governed by traffic emissions and it resulted in a high correlation between parameters (r^2=0.69-0.71). The correlation factor between LDSA and N for the whole campaign is very low at midday (r^2<0.25). This could be due to the fact that, as previously mentioned, nucleation processes may influence N concentrations in this period of the day, and a fraction of particles are probably too small to be detected by the LDSA monitor. Thus, small freshly formed nucleation mode particles are not detected by the NSAM and the fact that LDSA does not show the same decrease as BC during midday for some days of the period seem to be due to a change in particle size distribution during this period of the day. This is often the case when particles over the mixing layer, with a larger size, are mixed with the mixing layer air. This could also be due to an increase in accumulation mode particles following midday nucleation events, during which nucleation mode particles contribute to particle number but not to particle size. The best correlation between LDSA and PMx is obtained at midday and at night, with very similar correlation coefficients (r^2=0.59-0.67); this could be related to the lower impact of direct emission from sources which can affect particle mass and surface in a different way.

In order to better interpretet the relation between aerosol parameters is useful to clarify the behaviour of each parameter as a function of the particle diameter. Nickel et al. (2009) shows the size dsitribution in terms of number, surface area and alveolar surface area of particles from 10 to 1000nm (Figure A7.6). Maximum number of particles is obtained for particles diameters lower than 20nm, while the maximum surface area is obtained for particles diameters from 150 to 200nm.

The study of the ratios between parameters (Table A7.3) for the different periods of the day is also interesting for the characterization of aerosol processes and emission sources. As expected, at morning and evening rush-hours, ratios were very similar as all parameters are mainly related with traffic emissions. At midday, the ratio N/LDSA is at its highest, related with the enhanced secondary aerosol formation processes generating nucleation particles not detectable by the LDSA monitor. The PM_x/LDSA ratios were higher at midday than at rush-hours, pointing probably to the influence of increased resuspension processes by breeze on particle mass (Querol et al., 2001, 2005; Harrison et al., 2001; Charron and Harrison, 2005). The highest PM_x/LDSA ratios were registered at night, as conditions during this period are more favourable for coagulation and condensation processes, increasing the mass of particles with larger diameters and consequently smaller surface areas.

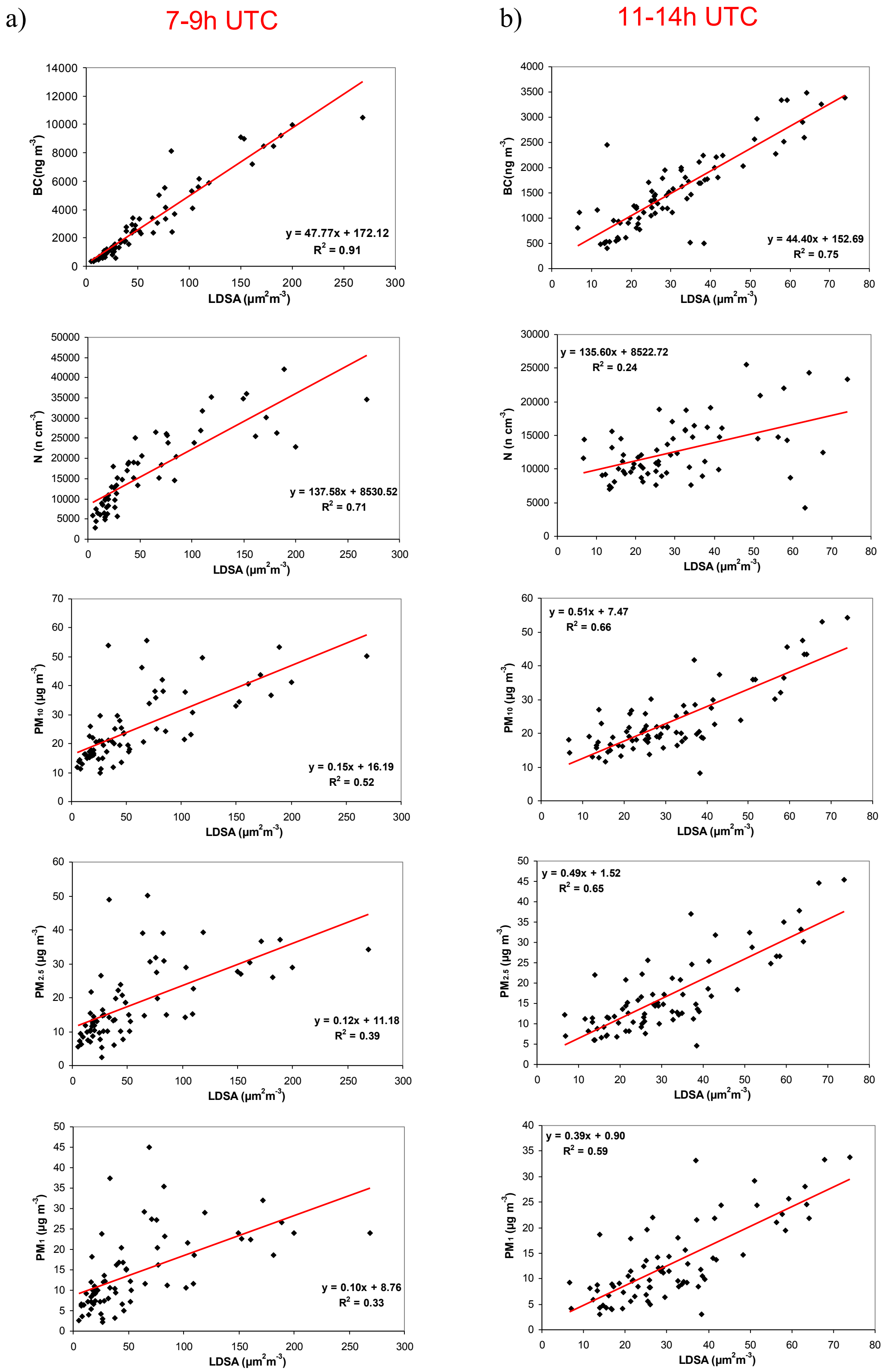

Figure A7.5. Correlations between LDSA and BC, N, PM_{10}, $PM_{2.5}$ and PM_1 for different periods of the day: a) 7-9, b) 11-14, c) 18-21 and d) 1-3h UTC.

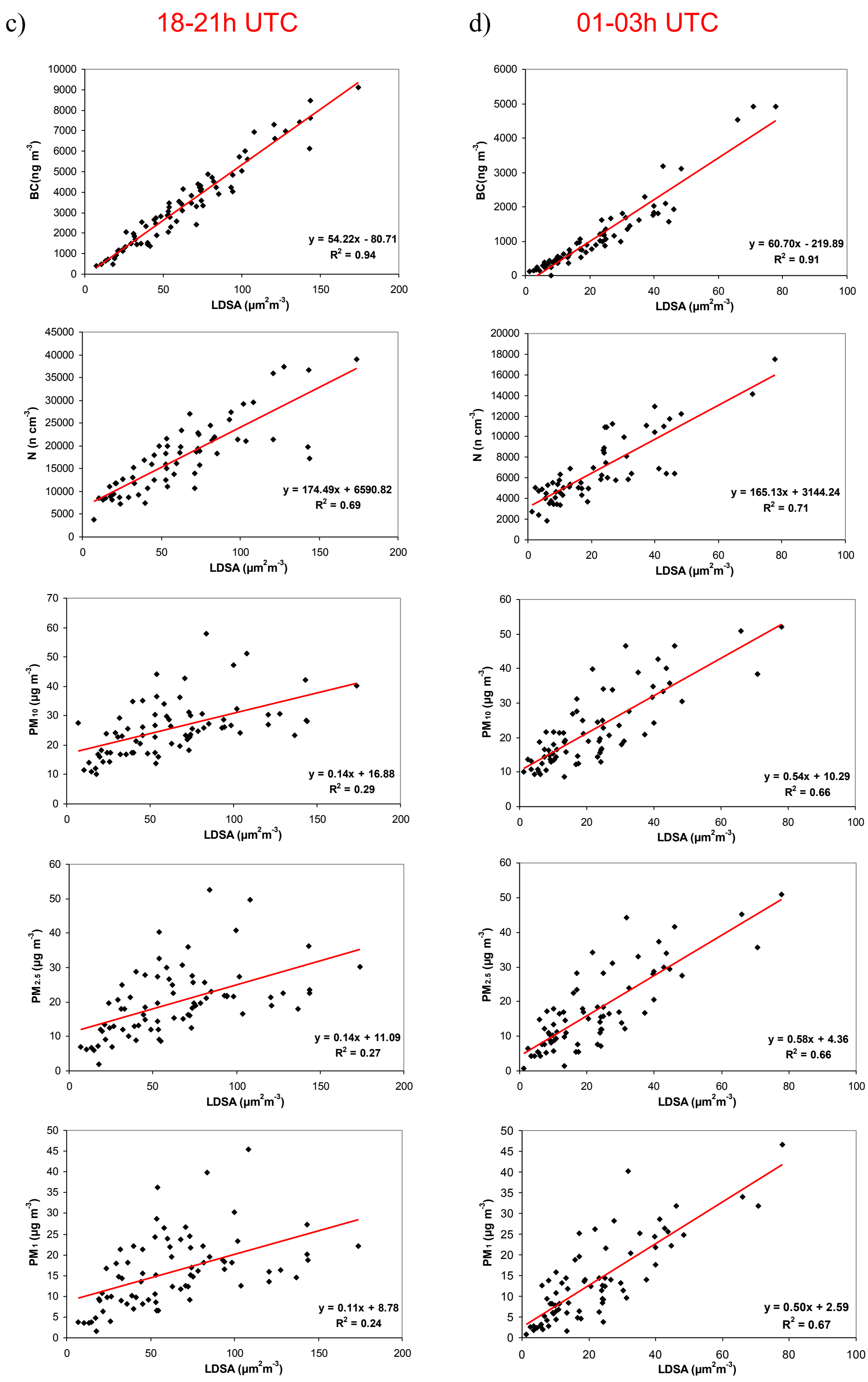

Figure A7.5. Continuation.

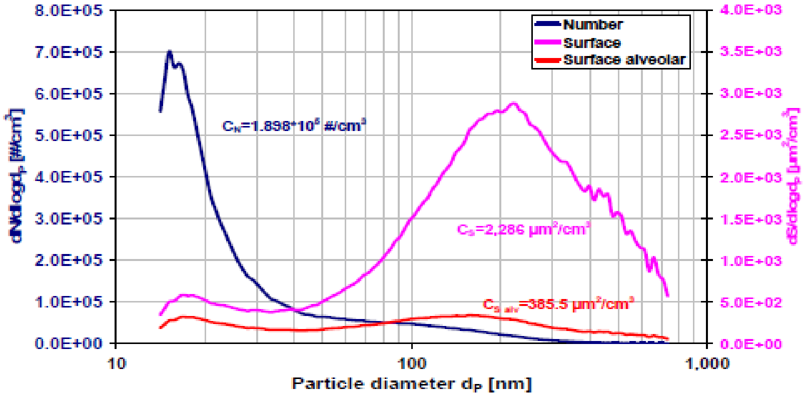

Figure A7.6. Size dsitribution of particles in terms of number, surface area and alveolar surface area of particles from 10 to 1000nm (Nickel et al., 2009).

Table A7.3. LDSA, BC, N, PM_{10}, $PM_{2.5}$ and PM_1 average values and LDSA/BC, LDSA/N and LDSA/PM_x ratios for the different periods of the day.

	Period of the day (Hour UTC)			
	7-9	11-14	18-21	1-3
LDSA ($\mu m^2 m^{-3}$)	54	33	62	23
BC (ngm^{-3})	2745	1604	3354	1171
N (ncm^{-3})	15578	12798	16655	6653
PM_{10} (μgm^{-3})	28	27	28	25
$PM_{2.5}$ (μgm^{-3})	20	19	21	19
PM_1 (μgm^{-3})	16	15	17	15

Ratio	Period of the day (Hour UTC)			
	7-9	11-14	18-21	1-3
BC/LDSA	51	48	54	50
N/LDSA	289	382	267	284
PM_{10}/LDSA	0.5	0.8	0.5	1.1
$PM_{2.5}$/LDSA	0.4	0.6	0.3	0.8
PM_1/LDSA	0.3	0.4	0.3	0.6

Earlier studies have shown the accurate application of diffusion chargers for ambient particle monitoring by demonstrating that they can be effectively used to derive the mean surface diameter with high temporal resolution in combination with a CPC (Bukowecki et al., 2002 and Ntziachristos et al., 2007). In accordance to these studies, the following equation was used within this study to estimate the mean surface diameter (ds, nm):

$$d_s = \left(\frac{S_A}{0.01KeQN} \right)^{1/1.285} \qquad (1)$$

where S_A is the surface of particles depositing in the alveolar region of the human respiratory tract; K is the instrument calibration constant in the alveolar mode (Shin et al., 2007); e is the electronic charge (e = 1.6 × 10^{-19} coulomb); Q is the aerosol sample flow rate and N is the total particle number concentration.

The mean surface diameter (d_s; nm) is the mobility of a monodisperse aerosol with the same surface and number concentration as the actual aerosol.

Figure A7.7 shows the scatter plot of BC versus N and versus LDSA as a function of the surface diameter. The correlation between BC and N seems to be highly dependent on the size of the particles and three defined lines for three different size ranges could be observed. For the finest particles (d_s<30nm), N increases are not accompanied by increases in BC, that are in their lowest levels. This confirms that nucleation mode particles are responsible for the lack of correlation between BC and N observed outside the rush hours, as described in previous chapters. In the case of BC versus LDSA, the dispersion is much lower and the correlation doesn't seem to depend on the particle size.

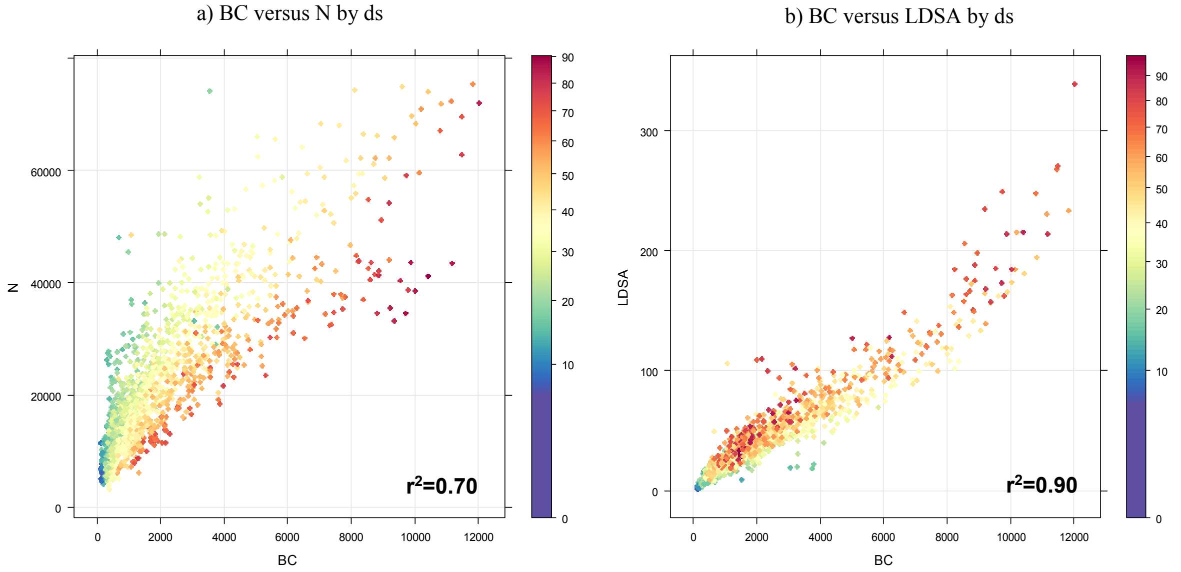

Figure A7.7. Scatter plots of BC (ngm^{-3}) and: a) N (ncm^{-3}) and b) LDSA (μm^{2}m^{-3}) as a function of ds (nm).

A7.2.3. Internal dose estimation

The alveolar deposited concentration multiplied by the breathing frequency, the tidal volume and the exposure time of a person allows the calculation of the internal dose. The dose was calculated for different respiratory parameters at Palau Reial urban background site. Exposure time is set to 3 hours for the time people spend outdoor in a working day. Information on the respiratory parameter for different level of exercise is derived fom literature (Table A7.4).

This kind of approach may be valuable for estimating personal doses in health studies, results are reported in Table A7.5, and they are in agreement with those reported in previous studies (Nickel et al., 2009; Kuhlsbuch et al., 2010).

Table A7.4. Respiratory parameters used in the ICRP Model (Hinds, 1999)

	Breathing Frequency (breaths/min)	**Tidal volume (cm^3)**
Female		
sitting	14	460
light exercise	21	990
heavy exercise	33	1360
Male		
sitting	12	750
light exercise	20	1250
heavy exercise	23	1950

Table A7.5. Dose for surface area for different respiratory parameters

	Surface area	
	Female	**Male**
Sitting	4.87E+07	6.80E+07
Light exercise	1.57E+08	1.89E+08
Heavy exercise	3.39E+08	3.39E+00

A7.3. CONCLUSIONS

A high correlation factor has been obtained between LDSA and BC concentrations (r^2=0.90), indicating that this parameter is strongly affected by traffic emissions. However, the relation between both parameters was weaker at midday (r^2=0.70), as the wind-dependency of both parameters differed. During the daytime, the levels of BC decreased markedly, while high values of LDSA could be obtained for wind velocities higher than 3.5m/s, which are usually reported at midday, indicating that a source other than traffic is also influencing the daily variation of LDSA levels. The factor responsible for this seem to be related with an increase in accumulation mode particles, probably following midday nucleation events during which nucleation mode particles contribute to particle number but not to particle surface. However, this process needs to be further studied in detail.

LDSA is an interesting and useful metric since it is an accurate indicator of potential negative health effects, as reported in previous studies (Oberdörster et al., 2005; Stoeger et al., 2006). Thus, correlations with other parameters, previously related with specific urban pollution sources, allow identifying major health adverse emission sources.

CHAPTER 8: Summarized results and discussion

8. SUMMARIZED RESULTS AND DISCUSSION

The investigation on urban air pollution sources carried out during this Thesis counted on extense instrumentation for the aerosol characterization period 2008-2011 and high time resolution data obtained within the DAURE intensive campaign. The results obtained for the specific urban environment of Barcelona (with high vehicle density, high temperatures and insolation, and prevalence of regional breeze circulatons) were compared with other European urban areas, and allowed us to contribute to improve the understanding on atmospheric pollutant sources and processes in urban environments. Results obtained within this work have provided evidence of the influence on different urban PM sources and factors, which affect the air quality in the city: road traffic, secondary aerosol formation processes, shipping emissions, construction-demolition works, industrial sources, biomass burning, city waste management, sea salt, resuspension and African dust.

Road traffic is the major source of concern in the city, governing the daily cycle of a number of parameters but mainly BC concentrations (chapter 3), which may be proposed as a vehicle exhaust emissions tracer to be potentially included in urban air quality control networks. BC levels vary proportionally to those of traffic-related gaseous pollutants (CO, NO and NO_2), and due to this high correlation, one may suppose that monitoring the levels of these gaseous pollutants would be enough to extrapolate exposure to BC concentrations. However, the BC/CO, BC/NO_2 and BC/NO ratios vary widely depending on the specific characteristics of urban sites, as a function of the distance to traffic, the vehicle fleet composition and age, and the influence of other carbonaceous sources such as biomass burning (chapter 4).

We conclude that a complete study of the impact of vehicle emissions on urban air quality would require the combination of BC and PM_{10}, as the latter is highly governed by non-exhaust particulate emissions resuspended by traffic (brake, tyre and pavement abrasion) (chapter 4).

The source apportionment analysis carried out within this work estimate an annual contribution of the sum of traffic exhaust and non-exhaust emissions of about 38% to PM_{10}, 38% to $PM_{2.5}$ and 46% to PM_1 mass concentrations (chapter 6 and 7). In accordance to this mass assessment analysis, the cancer risk estimate contribution was calculated from exposure as the sum of the cancer risk of all available species in this source following the methodology of Wu et al. (2009). As a result of this analysis of health risk, the road dust contribution to total cancer risk was estimated to be 50%

higher than the contribution to total mass for all PM fractions. This could not be observed for the exhaust fraction of vehicle emissions since VOCs concentrations could not been included in the investigation. These compounds have been reported to be the responsible for the elevated cancer risk of exhaust emissions in previous studies (Sax et al., 2006; Wu et al., 2009) and during the DAURE campaign, the time variation of these compounds in Barcelona showed a strong association with traffic emissions. Thus, further investigation in this direction is recommended (chapter 7).

Particle number concentrations (N) were also highly correlated with traffic emissions. The results of the N variability in Barcelona during 2009 were compared with those of other six selected urban areas covering road traffic, urban background, urban industrial and urban-shipping environments from southern, central and northern Europe. The evaluation of the hourly variability of levels of N, and the comparison with those of BC, indicated a narrow variation of primary road traffic N/BC ratios (minimum N/BC ratio, assuming the accuracy of BC to trace primary traffic emissions) during traffic rush hours, while a wide variation of this ratio was determined for the noon period among the different urban sites. In central and northern European urban sites, N levels tend to vary simoultaneously with BC levels during the whole day, while in southern Europe maximum N levels coinciding with minimum BC levels were usually recorded at midday as observed in this work. Thus, a source other than traffic is potentially influencing N and it has been attributed to midday **secondary new aerosol formation by nucleation** enhanced by photochemistry**,** occurring when atmospheric pollutants are diluted and maximum insolation occurs. Therefore, we concluded that N variability in different European urban environments is not equally influenced by the same emission sources and atmospheric processes (chapter 4).

The nucleation origin of the midday particles concentrations was supported by means of an SMPS deployed during the DAURE campaign. The wind-dependency of the size distribution for different size ranges was investigated, obtaining that the smaller particles, especially those in the nucleation mode (<20 nm) were detected in higher concentrations for wind velocities above 2.5 m/s, which mostly occurred at noon during this measurement period (sea-breeze circulation). Conversely, for particles above 50 nm the same wind-dependency than that shown by BC was obtained, with maximum values coinciding with minimum wind velocities, favouring the accumulation of pollutants (chapter 3).

In each of the considered environments, N data were also analysed in search for the primary emission of vehicle exhaust (N1) and the secondary parts from gaseous precursors, primary particles from non-traffic sources, and/or particles inherited in the air mass (N2). Thus, the N2 fraction in Barcelona accounted for 54% of number concentration on an annual basis, increasing up to 70% at midday, being this value about 85% during summer. These percentages were almost constant during all day for urban environments in central and northern Europe. The factors proposed to be responsible for the enhanced secondary particle formation observed in sourthern European cities at midday were: 1) increased solar radiation, 2) increased boundary layer height, 3) dilution of pollutants by the breeze, due to the coastal influence in the selected cities and 4) the high input of SO_2 from a source different to traffic exhaust and associated with breeze. However, considering the relatively high concentrations of SO_2 in some central and northern European cities, it can be stated that higher concentrations of SO_2 as gaseous precursor 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) seems to be essential (chapter 4).

The first LDSA measurements in the urban environment of Barcelona, set to detect the alveolar response, showed a high correlation with the BC measurements (r^2=0.90), thus linking traffic with high particle surface area concentrations (chapter 7). Particle surface is the area where interactions with the body take place (Maynard et al., 2005; Fissan et al., 2007).

Results showed both in terms of number of particles and in terms of mass concentration that secondary particles are exerting a significant influence on the air quality of Barcelona. A high contribution of secondary inorganic aerosols (NO_3^-, SO_4^{2-}) levels was registered in Barcelona with respect to other Spanish and European cities in previous works (Querol et al., 2008). These findings motivated the characterization of urban NH_3 levels and sources (chapter 5), since this compound is defined as the main responsible for secondary inorganic particulate matter formation in the atmosphere through the reactions with sulphuric and nitric acids (Seinfeld and Pandis, 1998).

This investigation on NH_3 levels and sources showed concentrations of NH_3 in Barcelona that reached 10.6 µg m^{-3} on average at urban background sites and 7.6 µg m^{-3} at traffic sites during summer, probably indicating the impact of emissions from biological sources, such as humans, sewage systems and garbage containers. In contrast, concentrations were higher at traffic sites (4.6 µg m^{-3}) than at urban background sites

(3.9 µg m^{-3}) during winter. The comparison of these levels with those registered in other European cities, showed that average concentrations in summer were far above average in European urban environments, which coupled with a high relative humidity could be responsible for a high contribution of NH_4-bearing species to the atmosphere (chapter 5). This would explain the higher NO_3^- levels registered in Barcelona with respect to other Spanish cities, such as Madrid, despite the higher traffic volume. Part of the difference between $PM_{2.5}$ levels in Madrid and Barcelona is due to NH_4NO_3 levels, high NH_3 levels in Barcelona could cause an increase of about 4 µg m^{-3} to the annual $PM_{2.5}$ mean.

The study of the spatial distribution of ambient NH_3 concentrations highlighted the historical city centre as the most polluted area, with mean levels reaching locally more than 30 µg m^{-3} in summer. The most important control factor on these elevated levels seemed to be the emissions from garbage containers, but also the urban design of this historical area, characterised by very densely populated narrow streets, which hinder the renewal or air masses and favour the accumulation of locally derived air pollutants (chapter 5).

Source-specific campaigns were designed in the city to identify the main controlling factors of NH_3 levels. The impact of vehicular traffic emissions on NH_3 emissions was assessed in one of the main traffic avenues of the city. A decrease in NH_3 levels of over 55% was observed as little as 50 m away from the highway, confirming vehicles as an important source. On the other hand, the study of NH_3 concentrations by districts of the city allowed us to obtain a correlation between this pollutant and the number of **garbage containers** per hm^2. This relation was high in summer and in winter (r^2=0.87 in summer and r^2=0.78 in winter) and shows an important impact of this source. Thus, urgent efforts are needed to better control and reduce the emissions from garbage collection systems in Barcelona, a city where the high population density together with the presence of periods of high temperatures and humidity turn waste disposal into a particular problem for air quality management. The sewage system was also studied although we feel that still further research is needed for more robust conclusions to be obtained (chapter 5).

Shipping emissions were traced in Barcelona by means of SO_2 concentrations, which peak at a different time to other gaseous pollutants owing to the regular daytime onshore breeze bringing harbour emissions at midday towards the city (chapter 3). Therefore SO_2 can be stablished as the best tracer of breeze circulations in Barcelona, transporting pollutants from the coastal area of the city to the monitoring site. Although their time variation and wind-dependendcy, correlating with that of the finer particles, pointed to sulphuric acid as the main responsible precursor of new secondary particle formation by reacting with NH_3, further research is needed to conclude their role, since a high correlation between SO_2 and N2 has not been found within this study (chapter 3). Indeed, on-line data of SO_4^{2-} and NO_3^- obtained during the DAURE campaign by the ToF-HR-AMS showed a significant agreement between N2 and NO_3^- during days affected by Atlantic advection, while this agreement was not found between N2 and SO_4^{2-}. Nevertheless, it is difficult to obtain conclusions through these considerations, as we are comparing parameters in different terms (number vs. mass) and the AMS does not detect particles lower than 50nm.

The evaluation of the coarse aerosol ($PM_{2.5-10}$) daily cycle during the DAURE campaign provided evidence on the influence of **construction-demolition works** on air quality by the detection of a PM peak between 10:00-14:00 h UTC, superimposed on the predictable daily patterns of the finer PM fracion that depend on traffic emissions. This daily maximum was ascribed to the emissions from the large number of construction and demolition works in the metropolitan area of Barcelona in 2009. Indeed, the number of works to be carried out between the end of 2008 and 2009 (1314 licenses) was 20% higher than the average for the period 2004-2008 (1061). These emissions are resuspended at midday by the highest wind speeds recorded at these times. The mineral matter content of this source is similar to that of traffic resuspension, regional dust or Saharan dust, so it was not possible to attribute all the increase in $PM_{2.5-10}$ at midday to the construction/demolition source, but also to road dust. This should be considered a maximum value. However, low levels of traffic tracers (Ba, Sn, Sb, Cu) in the coarse fraction were registered during the midday peak, the opposite of what happened in the case of Ca and S considered as the main tracers of construction works (Kim and Hopke, 2007; Karanasiou et al., 2009; Bernardoni et al., 2011).

Since carbonaceous matter has been reported to be a major constituent (up to 80%) of atmospheric aerosols in urban areas (Rogge et al., 1993; Pakkanen et al., 2000; Harrison et al., 2004), we found important to also characterize potential aerosol sources other than traffic. **Biomass burning** emissions have been defined as a significant contributor to PM levels in central and northern European cities (Puxbaum et al., 2007; Lanz et al., 2010), previous studies account for a contribution of up to 80% from wood combustion in Oslo (Larssen et al., 2006) while in Denmark wood burning represented around 47% of all Danish $PM_{2.5}$ emissions (Palmgren et al., 2005). Biomass burning contribution was expected to be much lower in Barcelona, but despite this and because of the scarce studies in the Mediterranean basin, an investigation on the biomass burning contribution to the particulate matter mass was carried out. The impact of the biomass burning source was detected by means of tracers such as levoglucosan, K^+ and OC. The high correlation between levoglucosan and OC (r^2=0.77) and K^+ (r^2=0.65), as well as a marked day/night variability of the levoglucosan and levoglucosan/OC ratios, showed the contribution from regional scale biomass burning emissions during night-time transported by land breezes. The quantification of biomass burning aerosols to PM levels on an annual basis was possible by means of the PMF model with the scripting ME-2, obtaining an annual contribution of 3% on average to PM_{10} and $PM_{2.5}$ levels and of 5% to PM_1 concentrations. Annually, biomass burning emissions accounted for 19%-21% of OC levels in PM_{10}, $PM_{2.5}$ and PM_1. The contribution of this source to K^+ ranged between 48% for PM_{10} to 97% for PM_1 (annual mean). Results for K^+ from biomass burning evidenced that this tracer is mostly emitted in the fine fraction, and that coarse K^+ should not be taken as an appropriate tracer of biomass burning (chapter 6). Therefore, important differences between European countries have been obtained regarding biomass burning emissions due to meteorological factors and human habits (Saarikoski et al., 2008), indicating that different national policies and control strategies might be needed to achieve a reduction of carbonaceous aerosol levels on a continental scale, if biomass burning emissions are targeted.

Finally, the potential health impact of the air pollution in Barcelona was investigated evaluating the ROS-generation capacity of the particulate matter in two different size fractions ($PM_{2.5-10}$ and $PM_{0.1-2.5}$) by means of two complementary assays, the Plasmid Scission Assay (PSA) and the Dichlorofluerescein Assay (DCFH) (chapter 7). The PSA test allowed for the obtention of the TD_{50} parameter (the dose of PM which is able to damage 50% of a plasmid DNA molecule). The average TD_{50} values obtained within this evaluation showed $PM_{0.1-2.5}$ samples (32 µg ml^{-1}) to be more toxic than the $PM_{2.5-10}$ fraction (130 µg ml^{-1}). This indicator of toxicity did not appear to be strongly dependent on the three different meteorological scenarios analysed (AT: Atlantic Advection, NAF: North African Saharan intrusion, and UP: Local pollutant accumulation under stagnant conditions). TD_{50} values reported in Barcelona were in the range of previous studies in highly polluted urban areas, such as urban landfills or industrial areas in Wales (UK) (Moreno et al., 2004; Senlin et al., 2008; Koshy et al., 2009).

No high associations were obtained between the concentration of a specific transition metals or specific emission sources and the percentage of damaged DNA; this perhaps being due to the fact that the redox activity of PM-associated metals depends not only on their concentration but also on their bioavailability and oxidation state (Nawrot et al., 2009). These findings seemed to indicate that the main controlling factor of aerosol toxicity in the city of Barcelona was particle size, probably related with the available surface area of the particles (chapter 7). Further studies are needed in order to elucidate which is the role of the chemical composition.

The use of the oxidant-sensitive probe DCFH in this study and the correlation with the PSA test results was useful to validate the results from the test and to cofirm the relation between the generation of ROS and the DNA damage response.

CHAPTER 9: Conclusions

9. CONCLUSIONS

The main conclusions from this thesis are:

-BC is proposed as a vehicle exhaust emissions tracer to be added to the urban air quality control networks. BC is a robust tracer of vehicle exhaust emissions which, combined with PM_{10}, could provide accurate estimates of traffic contributions to urban air quality. The BC/CO, BC/NO_2 and BC/NO ratios vary widely depending on the characteristics of different urban sites.

-N variability in different European urban environments is not equally influenced by the same emission sources and atmospheric processes. Whereas in northern and central European urban environments, N is dominated by vehicular exhaust emissions, in south Europe it is also influenced by midday photochemical nucleation events.

-Secondary particles exert a significant influence on the air quality of Barcelona, with nucleation processes governing the daily evolution of N. At noon, around 70% (up to 85% in summer) of total N is related with secondary formation processes. This maximum is associated with the development of the sea breeze circulation transporting gaseous precursors inland and contributing to the dilution of traffic-related pollutants.

- The high levels of NH_3 registered in Barcelona seem to explain the mass contribution of secondary inorganic particles to PM (mostly nitrate), which is significantly high compared with other Spanish and European cities. The levels of NH_3, of particularly concern during summer, appear to correlate with the number of garbage containers. Precursors gas transport due to the dynamics of winds in the city, indicated the potential implication of NH_3 in the significant secondary aerosols formation at midday.

-Shipping emissions are potentially implicated in the enhanced secondary aerosol formation at midday due to the SO_2 being transported from the coast inland to the monitoring site by the sea breeze circulation.

-Construction-demolition activities in Barcelona may increase hourly $PM_{2.5-10}$ levels by up to 8 $\mu g\ m^{-3}$ on an annual mean value based on hourly averages.

-Regional scale biomass burning emissions were detected in the Barcelona urban environment by means of levoglucosan, K^+ and OC, despite the low contributions in terms of mass and the typically complex atmospheric scenario found in the Mediterranean basin. This source didn't show a significant contribution to urban PM_x levels (3-5%) and it was associated to anthropogenic residential and agricultural biomass burning activities in surrounding rural areas. This is contrary to what is observed in central and northern European cities.

-The health impact of the urban aerosols in the atmosphere of Barcelona according to the ROS-generating capacity of $PM_{2.5-10}$ and $PM_{0.1-2.5}$ samples seemed to be mostly controlled by the PM size fraction, probably related with the available surface area of the particles. Further investigation on the role of the chemical composition is needed.

CHAPTER 10: Future Research and open questions

10. FUTURE RESEARCH AND OPEN QUESTIONS

The research carried out in this study leaves many open questions that may lead to additonal research directions in urban environments in the Western Mediterranean Basin.

- It is highly interesting to keep operating the urban background monitoring site in Barcelona in order to extend the time series, as this will allow understanding the influence of changes in emissions sources (e.g. a reduction in industrial emissions has been observed in recent years, possibly associated with the economical crisis; the impact of construction-demolition activities in 2009 was detected due to a change in the daily cycle of the coarse PM fraction), the impact of new technological measures implemented to abate vehicle emissions, as well as the effect of variabilities in meterological conditions.

-The simultaneous analysis of long time series of air pollutants, including new parameters such as size segregated N, BC or LDSA, and mortality will allow investigating in modifying the association between parameters.

- The measurements and interpretation of on-line NH_3 levels within the different seasons will be essential to conclude on the contribution of this pollutant in the processes of secondary inorganic aerosol formation. It will allow elucidating the role of NH_4NO_3 levels in the annual $PM_{2.5}$ mean difference ($4 \mu g\ m^{-3}$) between Barcelona and Madrid. In addition, the city waste management impact on NH_3 concentrations needs more investigation, as well as the emission factors of NH_3 by vehicular traffic.

- The chemical characterization of nucleation processes and subsequent particle growth is highly relevant to be resolved considering the high contribution of secondary particles to particle number and mass.

- Shipping emissions should be assessed in detail to evaluate the precise mechanisms through which these emissions contribute to particle number and secondary aerosol formation in coastal urban environments.

-The implication of the VOCs in the formation of secondary organic aerosols has not been characterised. In addition, it would be interesting to obtain a long time-series to complete the risk assessment analysis carried out in this thesis.

-Further research will need to consider the incorporation of LDSA concentrations as a routine parameter in urban environments, as its high correlation with BC measurements is an indicator of the potential link between particle surface and respiratory diseases caused by traffic emissions. It will also be interesting to investigate the effect of meteorological changes by seasons on this health impact indicator. The estimation of the mean surface diameter by means of LDSA and N measurements will need to be correlated with data from a SMPS monitor.

- It is important to deeply analize the effect of cooking in the city, which according to Mohr et al., 2012 accounts for 13% of OC. The identified source presents a time variation different from the expected considering cooking habits in the city. It is also relevant to characterize other sources of non-fossil derived OC which have been quantifed in about 60% of total OC (Minguillón et al., 2011).

-Since traffic emissions have been concluded to be the main source in the urban environment of Barcelona due to the high vehicle density, one future aim should be to assess differences in commuters' exposure to traffic-related air pollution associated to transport mode, route, and fuel type, in order to suggest future air pollution mitigation strategies in the city.

-The study of the TD_{50} value representative of the $PM_{2.5-10}$ and the $PM_{0.1-2.5}$ fractions in Barcelona carried out in this Thesis has left open questions with regard to the role of the chemical speciation in the ROS-generation capacity of PM samples. A complete annual time-series of this indicator will help to understand the main parameters implicated in the potential of urban PM samples to cause oxidative stress responses.

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ANNEX I. Presentations in scientific meetings

The results obtained in this thesis were presented in scientific meetings in form of poster and oral presentations.

Reche, C., Moreno, T., Viana, M., Querol, X., Alastuey, A., Pérez, N., Amato, F., Moreno, N. Causes of particulate matter variability in a Mediterranean urban site: road traffic, photochemistry and resuspension. Air Pollution and Health Presented by the American Association for Aerosol Research. San Diego, CA, March 22-26, 2010. Presentation: Poster presentation.

Viana, M., Díez, S., Alastuey, A., Querol, X., **Reche, C.**, 2010. Workplace exposure to traffic-derived nanoscaled particulates. Nanosafe 2010: International Conference on Safe production and use of nanomaterials. Grenoble, Francia, 16-18/11/2010. Oral presentation.

Pandolfi, M., Cusack, M., Pey, J., Alastuey, A., Querol, X., **Reche, C.**, Moreno, T., Viana, M., Jimenez, J.L., 2010. Intensive Aerosol Measurements during the DAURE Campaign at a Eusaar Rural Site in NW Mediterranean. IAC 2010 Helsinki Finland, 31 Aug-3 September 2010. Poster presentation.

Karanasiou, A., Moreno, T., Amato, F., Lumbreras, J., Borge, R., Narros, G.A., **Reche, C**., Pey, J., Tobias A., Alastuey, A., Querol, X., 2010. Estimation of the road dust contribution in the urban aerosol. IAC 2010 Helsinki Finland, 31 Aug-3 September 2010. Poster presentation.

Reche, C., Moreno, T., Viana, M., Querol, X., Alastuey, A., Jimenez, J.L.,Pandolfi, M., Amato, F., Pérez, N., Moreno, N. Causes of daily cycle variability of atmospheric pollutants in a western Mediterranean urban site (DAURE campaign). Vol. 12, EGU2010-12313, 2010. EGU General Assembly 2010. Poster presentation.

Minguillón, M.C., Perron, N., Querol, X., Szidat, S., Fharni, D., Wacker, L., **Reche, C**., Cusack, M., Baltensperger, U., Prévôt. A.S.H. Carbonaceous particulate matter in the Western Mediterranean Basin: contribution of fossil versus modern sources. International Aerosol Conference IAC 2010. Abstract number 894. Helsinki, Finland, 29 August - 3 September 2010. Poster presentation.

Amato, F., Viana, M., Richard, A., Furger, M., Prévôt, A.S.H., Nava, S., Lucarelli, F., Querol, X., Alastuey, A., **Reche, C.**, Moreno, T., Pandolfi, M., Pey, J. Size and time-resolved roadside enrichment of atmospheric particulate pollutants. Geophysical Research Abstracts 2011 EGU General Assembly 2011. Poster presentation.

Reche, C., Querol, X., Viana, M., Moreno, T., Pey, J., Dall'Osto, M., Alastuey, A., Rodríguez, S., González, Y., Fernández-Camacho, R., de la Rosa, J., Prévôt, A.S.H., Hueglin, C., Harrison, R.M., Quincey, P. Variability of levels of PM, black carbon and particle number concentration in selected European cities. Geophysical Research Abstracts Vol. 13, EGU2011-12304. EGU General Assembly 2011. Poster presentation.

Reche, C., Viana, M., Amato, F., Querol, X., Moreno, T., Minguillón, M.C., Alastuey, A., Hillamo, R., Tenillä, K., Saarnio, K., Seco, R., Mohr, C. P-0764. Biomass burning contributions to urban aerosols in a coastal Mediterranean city. International Society for Environmental Epidemiology, 13-16 September 2011. Barcelona. Poster presentation.

Reche, C., Viana, M., Pandolfi, M., Amato, F., Querol, X., Moreno, T., Alastuey, A., Karanasiou, A., Ripio, A., Pérez, N., Cusack, M., Minguillón, M.C. Ammonia emissions in a Mediterranean urban environment. European Aerosol Conference, EAC 2011. Manchester, 4-9 September 2011. Poster presentation

Karanasiou, A., Moreno, T., Amato, F., Lumbreras, J., Narros, A., Borge, R., Tobías, A., Boldo, E., Linares, C., Pey, J., **Reche, C.**, Alastuey, A., Querol, X. Road dust resuspension and chemical composition with regards to street washing activities. V Reunión Española de Ciencia y Tecnología de Aerosoles – RECTA 2011. Madrid. Poster presentation.

ANNEX II. Related publications

The results obtained within this study have motivated the following publications:

Pey, J., Pérez, N., Querol, X., Alastuey, A., Cusack, M., **Reche, C.**, 2010. Intense winter atmospheric pollution episodes affecting the Western Mediterranean. Science of The Total Environment, 408, 8, 1951-1959

Pérez, N., Pey, J., Cusack, M., **Reche, C.**, Querol, X., Alastuey, A., Viana, M., 2010. 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 Science and Technology, 44, 487-499.

Viana, M., Díez, S., **Reche, C.**, 2011. Indoor and outdoor sources and infiltration processes of PM_1 and black carbon in an urban environment. Atmospheric Environment, 45, 35, 6359-6367

Amato, F., Viana, M., Richard, A., Furger, M., Prévôt, A.S.G., Nava, S., Lucarelli, X., Querol, X., Alastuey, A., **Reche, C**., Moreno, T., Pandolfi, M., Pey, J., 2011. Size and time-resolved roadside enrichment of atmospheric particulate pollutants. Atmospheric. Chemistry and Physics, 11, 453-483, 2011.

Reche, C., Viana, M., Moreno, T., Querol, X., Alastuey, A., Pey, J., Pandolfi, M., Prévôt, A., Mohr, C., Richard, A., Artiñano, B., Gomez-Moreno, F.J., Cots, N., 2011. Peculiarities in atmospheric particle number and size-resolved speciation in an urban area in the western Mediterranean: Results from the DAURE campaign. Atmospheric Environment, 45, 30, 5282-5293.

Moreno, T., Querol, X., Alastuey, A., **Reche, C**., Cusack, M., Amato, F., Pandolfi, M., Pey, J., Richard, A., Prévôt, A.S.H., Furger, M., Gibbons, W., 2011. Variations in time and space of trace metal aerosol concentrations in urban areas and their surroundings. Atmospheric Chemistry and Physics, 11, 9415-9430.

Reche, C., Querol, X., Alastuey, A., Viana, M., Pey, J., Moreno, T., Rodríguez, S., González, Y., Fernández-Camacho, R., Sánchez de la Campa, A. M., de la Rosa, J., Dall'Osto, M., Prévôt, A. S. H., Hueglin, C., Harrison, R. M., and Quincey, P., 2011. New considerations for PM, Black Carbon and particle number concentration for air quality monitoring across different European cities. Atmospheric Chemistry and Physics, 11, 6207–6227.

Minguillón, M.C., Perron, N., Querol, X., Szidat, S., Fahrni, S.M., Alastuey, A., Jimenez, J.L., Mohr, C., Ortega, A.M., Day, D.A., Lanz, V.A., Wacker, L., **Reche, C**., Cusack, M., Amato, F., Kiss, G., Hoffer, A., Decesari, S., Moretti, F., Hillamo, R., Teinilä, K., Seco, R., Peñuelas, J., Metzger, A., Schallhart, S., Müller, M., Hansell, A., Burkhardt, J.F., Baltensperger, U., Prévôt, A.S.H., 2011. Fossil versus contemporary sources of fine elemental and organic carbonaceous particulate matter during the DAURE campaign in Northeast Spain. Atmospheric Chemistry and Physics, 11, 12067-12084.

Mohr, C., DeCarlo, P.F., Heringa, M.F., Chirico, R., Slowik, J.G., Richter, R., **Reche, C.**, Alastuey, A., Querol, A., Querol, X., Seco, R., Peñuelas, J., Jiménez, J.L., Crippa, M., Zimmerman, R., Baltensperger, U., Prévôt, A.S.H., 2012. Identification and quantification of organic aerosol from cooking and other sources in Barcelona using aerosol mass spectrometer data. Atmospheric Chemistry and Physics, 12, 1649-1665.

Reche, C., Moreno, T., Amato, F., Viana, M., L. van Drooge, B., Chiang, H.-C., Bérubé, K., Jones, T., Alastuey, A., Querol, X., 2012. A multidisciplinary approach to characterise exposure risk and toxicological effects of PM_{10} and $PM_{2.5}$ samples in urban environments. Ecotoxicology and Environmental Safety, In Press, Corrected Proof, Available online 16 December 2011.

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