# 7. Conclusions

**PM events and seasonal evolution**

The analysis of PM10 and TSP time series recorded from 1996 to 2000 at nineteen rural, urban and industrial sites in Eastern Spain reveals that day-to-day variations in PM levels are highly influenced by meteorology. From March to October PM levels at rural, urban and industrial sites vary as a function of the concatenation of Atlantic episodes (Atlantic air mass advections with low PM levels) and Regional events (transport of pollutants from urban/industrial to rural sites) resulting in low and high PM events, respectively. From November to February low PM levels are recorded at rural sites and variations in PM levels at urban/industrial sites are governed by the successive occurrence of Atlantic episodes and Local urban/industrial pollution events. The African dust outbreaks occur from January to October and induce very high PM levels in all the environments.

African dust outbreaks over Eastern Spain occur under meteorological scenarios that are characterised by a depression located to the West or Southwest of Portugal (most frequently in January-June period) and/or by an anticyclone located to the East or Southeast of the Iberian Peninsula (most frequently in July-August, and sometimes in March). Approximately 10 African events per year with a mean duration of 3 days occur in Eastern Spain. Heavy dust outbreaks were identified in March in 3 of the 5 years studied. Mean PM10 and TSP levels during African dust events were in usually in the range 25-38µg/$m^3$ at rural and 40-60µg/$m^3$ at urban sites. At a rural site, daily mean levels >50µgPM10/$m^3$ were recorded for 1-7µg/$m^3$ days per year during African episodes.

Regional episodes occur under a synoptic meteorological context characterised by weak baric gradient conditions over the study area, which is frequently associated with the Iberian thermal low development in summer. These Regional PM events are associated with ozone episodes. In these events the breeze circulation induces the transport of particulate pollutants from the urban/industrial to the rural sites, and the development of meso-scale circulations inhibits the air mass renovation and favours the accumulation of PM in the regional atmosphere. Approximately 12 Regional events per year with a mean duration of 4-6 days occur in Eastern Spain. Mean PM10 and TSP levels were in the range 20-30µg/$m^3$ for the spring and autumn and in the range 20-45µg/$m^3$ for the summer Regional events at rural sites. At urban sites mean PM10 and TSP levels were in the range 32-52µg/$m^3$ during these episodes.

Local urban episodes are typically observed under anticyclonic situations during the cool seasons. These high PM levels at the urban sites are associated with high NOx and CO levels. Mean PM10 and TSP levels during Local urban pollution episodes were in the range 35-52µg/$m^3$ at urban and in the range 10-15µg/$m^3$ at rural sites.

The Atlantic episodes occur under several meteorological scenarios and are typically associated with cold fronts and rain. Mean PM10 and TSP levels during Atlantic events were in the range 10-15µg/m$^3$ at rural and 25-43µg/m$^3$ at urban sites.

At rural sites PM levels undergo a seasonal evolution characterised by a summer maximum, which is caused by the high frequency and intensity of Regional PM episodes and by the occurrence of intensive African dust events. The difference between the urban and rural PM concentrations is characterised by an autumn-winter maximum owing to the frequent Local urban pollution episodes.

The frequent occurrence of African and Regional PM episodes has implications for air pollution regulation strategies and accounts for the marked difference in the features of the airborne particulates between Southern and Northern Europe. The African dust events are more frequently observed in Mediterranean countries than in Central-Northern Europe. Regional PM episodes are caused by the specific orography and prevailing meteorology in the Western-Central Mediterranean which inhibit the air mass renovations favouring the airborne particulate accumulation in the regional atmosphere. In contrast, Central-Northern Europe is affected by the westerly mid-latitude general circulation frequently associated with cold fronts and rain which favour air mass renovations and scavenging. When comparing two regions with the same degree of urban/industrial development (similar emission rates of air pollutants) in the Western Mediterranean and in Central-Northern Europe, higher background levels of airborne particulate pollutants are expected in the Mediterranean region because of the smaller “self-cleaning” capacity of the Mediterranean atmosphere.

**Chemical characterisation of PM**

The analysis of PM10 and TSP size segregated fractions in the cascade impactor samples collected at rural (MONAGREGA in the Ebro basin), urban (L’HOSPITALET in the Barcelona Metropolitan Area) and ceramic production (ONDA in Castelló area) sites as well as PM2.5 samples collected at the urban (L’HOSPITALET) site revealed that the PM composition undergoes significant variations throughout the year, which may be summarised as follows:

- High concentrations of natural mineral dust components (e.g. Al, Fe, Ti, Sr, Mg) are simultaneously recorded in PM10 and PM2.5 at the rural, urban and industrial sites during African dust outbreaks.
- At the urban site, mineral dust components mainly occur in the coarse fraction (2.5-10µm), except during African dust outbreaks, when levels of Al, Ca, Ti, Sr, Mg, and Fe also undergo a significant increase in PM2.5.
- An excess of Na with respect to the Na/Cl marine ratio in summer owing to the reaction of acid species with sea salt.
- High background levels of non-sea-salt (nss)-sulphate are recorded in summer at all sites. Nss-sulphate is mainly present as ammonium-sulphate in fine fractions (<1.5µm)

of PM, but minor amounts of calcium-sulphate are also observed in coarse fractions (1.5 to >25µm) of PM.

- Nitrate levels and grain size distribution exhibit a seasonal evolution. Maximum nitrate levels are attained in autumn-winter due to ammonium-nitrate formation because of its enhanced thermal stability in the cold season. In the warm season nitrate occurs as sodium and/or calcium nitrate. Ammonium-nitrate is in the finest size fractions (<1.5µm) of PM, whereas sodium/calcium-nitrate occur in both fine and coarse fractions. In the cold season around 80% of nitrate is found in the fine(<2.5µm) fraction, whereas in the warm seasons around 30% of nitrate occurs in the coarse (2.5-10µm). Moreover, daily cycles of nitrate with higher levels at night (owing to ammonium-nitrate formation at night and evaporation during daylight) are observed in summer at the rural site.
- At the urban site, carbon levels exhibit a seasonal evolution with an autumn-winter maximum, whereas at the rural site no significant seasonal trend is observed. At the rural site, the average content of organic, elemental and mineral carbon fractions accounted for 83%, 8% and 10% of total carbon in PM10, respectively. At the urban site these fractions of carbon account for 70%, 26% and 5% of total carbon in PM10, respectively. Around 82% of carbon in PM10 occurs in PM2.5 at the urban site.

**Source origins and contributions to PM10 and PM2.5 levels**

The source identifications was performed by Principal Component Analysis, whereas the source contributions were calculated by two receptor modelling techniques based on Multi-linear Regression Analysis (MLRA) and Mass Balance Analysis (MBA). The MLRA provides slightly higher contributions due to the fact that MBA is based on the distribution of the chemically determined PM-mass among the PM sources, whereas the MLRA takes into account unaccounted PM-mass (mainly water bounded to aerosol). The source contribution in this study is assessed by the two methods.

At the MONAGREGA rural site the PM10 annual mean is equal to 22µg/m$^3$, the main contributions being 6µg/m$^3$ (27%) from industrial emissions for power production, 5µg/m$^3$ (23% of PM10) of natural mineral dust, 3-5µg/m$^3$ (14-23%) from vehicle exhausts and 1-2µg/m$^3$ (5-9%) of sea spray.

At the L'HOSPITALET urban kerbside the PM10 annual mean is equal to 49µg/m$^3$, the main contributions being 17-22µg/m$^3$ (35-45%) from vehicle exhausts 12-15µg/m$^3$ (24-31%) from industrial emissions for power production, 12µg/m$^3$ (25% of PM10) of mineral dust and 2-3µg/m$^3$ (4-6%) of sea spray.

At the L'HOSPITALET urban kerbside the PM2.5 annual mean is equal to 34µg/m$^3$, the main contributions being 14-18µg/m$^3$ (41-53%) of vehicle exhaust products, 10-12µg/m$^3$ (29-35%) from industrial emissions for power production and 3-4µg/m$^3$ (9-11% of PM2.5) of mineral dust.

At the ONDA ceramic production background site, averaged five months (around summer) PM10 levels reached 33µg/m$^3$, the main contributions being 9µg/m$^3$ (27% of PM10) of mineral dust from clay treatment and from natural sources, 1-2µg/m$^3$ (3-6%) from other ceramics related activities, 9µg/m$^3$ (27%) from industrial emissions for power production, 2-3µg/m$^3$ (3-6%) of sea spray + petrochemical emissions and 5-6µg/m$^3$ (15-18%) from bio-mass burning.

At the rural and urban sites, the vehicle exhaust contribution to PM10 levels exhibit an autumn-winter maximum because of the seasonal trend of nitrate (and carbon at the urban site). The contribution of the industrial emissions to PM10 exhibit a high background in summer at all sites because of the seasonal trend of sulphate. The contribution from the industrial and vehicle exhaust emissions are very similar in PM10 and PM2.5 at the urban site. Local anthropogenic sources such as road dust and ceramic manufacture account for the higher levels of mineral dust at the urban and industrial sites than at the rural sites, respectively. High contributions of mineral dust are simultaneously recorded in PM10 at all sites during African dust events, and in a minor proportion in PM2.5 at the urban site.

During summer the Regional episodes at the rural site, PM10 is mainly constituted by secondary PM derived from industrial emissions (40-50% of PM10) and mineral dust (20% of PM10) from soil re-suspension processes. During Local urban pollution episodes in winter, vehicle exhausts is the most important source of PM10 (50-60%) and PM2.5 (45-60%) at the urban site. During African dust outbreaks the mineral dust load accounts for the largest fraction of PM10 (50-55% at the rural and 45-50% at the urban sites) and for a significant fraction of PM2.5 (30%).

**PM10 levels and EU standards**

The analysis of the 1996-2000 data yielded annual mean PM10 levels of 17-20µg/m$^3$ at rural, 30-45µg/m$^3$ at urban and 45-60µg/m$^3$ at industrial sites. PM10 levels at rural sites are only slightly lower than the 2010 EU annual PM10 limit value. It will not be easy to meet the 2010 EU PM10 standards at urban and industrial sites.

The natural load (natural mineral dust + sea spray) in PM10 is estimated at 6-7µg/m$^3$ at MONAGREGA (rural) and in 7-8µg/m$^3$ L'HOSPITALET (urban) sites, which accounts for 30-35% and 35-40% of the 2010 EU annual PM10 limit value, respectively.

At the L'HOSPITALET urban site, the contribution of the vehicle exhausts (estimated at 17-22µg/m$^3$) already accounts for levels similar to the 2010 EU annual PM10 limit value.

Mineral dust concentrations during African dust outbreaks are in the range 20-30µg/m$^3$ in PM10 in all the environments. At the MONAGREGA rural site, the highest PM10 levels (>40µg/m$^3$) are recorded during African dust episodes, the natural mineral dust being the most important source. At the L'HOSPITALET urban kerbside, the highest PM10 levels are

mostly recorded during winter Local pollution episodes, the vehicle exhaust emissions being the most important source.

At rural sites, 2-5 exceedances of the EU daily PM10 limit value (50µg/m$^3$) are recorded every year during African dust outbreaks. Thus, the occurrence of the African dust outbreaks will render it difficult to meet the 2010 EU PM10 requirements for the permitted exceedances of the daily limit value of PM10, even at rural sites. A number of non-African induced exceedances occur every year at urban and industrial sites. At sub-urban sites, 2-8 African induced and 4-6 non-African induced exceedances of the EU daily PM10 limit value are recorded every year on average. At urban kerbside stations, around 15 African induced and 40-80 non-African induced exceedances of the EU daily PM10 limit value are recorded every year on average.

The location of the urban monitoring stations is a key factor when assessing PM10 levels. According to the EU Directive 1999/30/CE, the PM10 monitoring stations should be located in such as way as to avoid measuring very small micro-environments in the immediate vicinity. However, almost all the urban monitoring stations in Eastern Spain are located at kerbsides. Furthermore, Spanish cities are characterised by narrow streets with high buildings and a lack of open areas, which does not facilitate pollutant dispersions.

**Parameters for PM monitoring**

The analysis of PM10, PM2.5 and the TSP size segregated fractions shows that most of the PM derived from combustion occurs in PM2.5, with the exception of nitrate in summer. In contrast, anthropogenic primary PM emissions mainly affect the coarse fraction (2.5-10µm) of PM.

PM emissions derived from road traffic affect both fine (<2.5µm) and coarse (2.5-10µm) fractions of PM. In road traffic monitoring stations, PM2.5 is an indicator of PM resulting from vehicle exhaust emissions, whereas the 2.5-10µm fraction is mainly constituted by road dust. In the Barcelona Metropolitan Area, PM levels tend to increase during rush hours, the ratio PM2.5/PM10 being directly dependent on the road traffic density. The PM2.5/PM10 ratio reaches minimum values (~0.6) during the rush hours in the early morning and late afternoon and maximum values (~0.8) at noon and night. This is caused by traffic re-suspension of coarse road dust (2.5-10µm) in the rush hours and its subsequent sedimentation. Owing to this and to the longer residence time of fine particles, the amplitude of the daily cycle of TSP (~49µg/m$^3$) and PM10 (~37µg/m$^3$) is much higher than that of PM2.5 (~15µg/m$^3$) and PM1 (~13µg/m$^3$). Thus, PM10 levels are characterised by a higher variability ("higher noise") than that of PM2.5 and PM1.

In areas affected by secondary PM emissions, PM2.5 and PM1 are better tracers than PM10 for the impact of these anthropogenic emissions on the air quality due to the fact that the most relevant secondary PM species (sulphate, organic PM and a significant nitrate

fraction) occur in the fine fraction of PM. PM2.5/PM10 ratios experience significant variations around a large $SO_2$ emission source located in a rural context (Teruel power plant in the Ebro basin). Very high PM2.5/PM10 ratios are recorded (0.7-0.9) during fumigations of the $SO_2$ plume. At sites affected by the re-suspension of mineral dust due to natural causes, or by crop cultivation or grazing very low PM2.5/PM10 ratios are found (<0.2). A higher PM2.5/PM10 ratio is found in ambient air (0.4-0.7). PM1 proved to be the best indicator for detecting the fumigations of $SO_2$.

In areas where industrial activities result in primary coarse PM anthropogenic emissions (e.g. cement, ceramic manufacture or mining) PM2.5 is not an adequate parameter for monitoring air quality. In the case of the ceramic production area of Castelló, particulate emissions have a coarse grain-size distribution, resulting in very low PM2.5/PM10 ratios (~0.3) around most PM sources. The atmospheric transport induces a subsequent grain-size segregation which results in a lower PM2.5/PM10 ratio (~ 0.6) several kilometres from the ceramic production area.

The interference of the African dust in PM monitoring is considerably less in PM2.5 than in PM10. Mineral dust concentrations during African dust events are in the range 20-30µg/m$^3$ in PM10 and in the range 10-15µg/m$^3$ in PM2.5, which indicates a reduction of 50%. Nevertheless, PM2.5 is still influenced by this natural source. This influence is probably much less in PM1.