Chapter 2

Objectives of this study

2.1 Context and state of the art

Given the increasing number of epidemiological studies showing a close relationship between health and urban PM pollution in the last decade, a number of countries have reviewed their National Air Quality Standards for PM concentrations in ambient air. According to the World Health Organisation (WHO), some EU governments spend more than six thousand million euros/year (more than one billion pesetas/year) on hospitalisations including absence from work caused by the effects of urban PM pollution (WHO, 1999). Moreover, according to this organisation the annual number of deaths related to PM pollution due to vehicle exhaust may exceed that caused by road traffic accidents in Europe (WHO, 1999). In response to these adverse effects of air pollution, the EU Commission has revised the standards for several air pollutants, and has defined limit values for PM10 concentrations in ambient air (EU Directive 1999/30/EC). Emission abatement measures should be taken to meet the EU limit values. Given that a number of epidemiological studies indicate that the PM2.5 fraction may be responsible for the adverse effects of PM10 (e.g. Dockery et al., 1993; Swartz et al., 1996), the European Commission highlighted the importance of PM2.5 and drew attention to the scant information on PM2.5 levels and composition in Europe. Research into PM2.5 has been encouraged into the different EU regions. For the above reasons, the EU limit values for PM will still be subject to revision in 2003.

The EU standards introduce new parameters for PM monitoring since they are based on the measurement of PM10 concentrations and the previous Spanish standards were based on measurements of TSP and black smoke (Royal Decrees 1613/1985 and 1321/1992, BOE number 219 and 289 12/09/1985 and 02/12/1992, respectively, incorporation of the EU Directives 80/779/EEC and 89/427/EEC to the Spain, Table 2-1). The EU standards are based on daily and annual limit values for PM10 levels that become progressively more restrictive from 2001 to 2010. After January 1 2010, annual PM10 levels should not exceed 20µg/m^3, and the daily mean concentration of 50µg/m^3 should not be exceeded more than 7 days/year (98 percentile) in the EU.

Table 2-1. Ambient PM standards in Spain from 1992 to 2010

	Previous Standard	**New EU Standard**		
	1992-2001	*2001*	*2005*	*2010*
Parameter	TSP	PM10	PM10	PM10
I. *Annual limit value*	150 $\mu g \cdot m^{-3}$	46 $\mu g \cdot m^{-3}$	40 $\mu g \cdot m^{-3}$	20$\mu g \cdot m^{-3}$
II. *Daily limit value*	300 $\mu g \cdot m^{-3}$	70 $\mu g \cdot m^{-3}$	50 $\mu g \cdot m^{-3}$	50 $\mu g \cdot m^{-3}$
N. of exceedances allowed	18	35	35	7

The new standards for PM10 defined limit values for the whole of the European Union. However, such homogeneity in the maximum allowed PM10 concentrations applies to regions with different PM10 features. Spatial variations of PM10 levels and composition in Europe are governed by regional variations of: a) natural and anthropogenic particulate emissions, b) regional atmospheric dynamics controlling transport and dispersion of pollutants, and, c) ambient conditions (e.g. insolation, temperature, humidity) and levels of reactive gases (e.g. OH or O_3) influencing the gas to particle conversion. Many of these factors are very different in Southern and Central-Northern Europe. The main peculiarities of the Mediterranean countries concerning ambient PM are summarised below.

The contribution of crustal PM to ambient PM10 levels is expected to be higher in Southern than in Central-Northern Europe for the following reasons: a) the poor vegetal soil coverage in Mediterranean countries (Figure 2-2), and b) the frequent African dust outbreaks over Southern Europe. Thus, local soil re-suspension in Southern countries may significantly contribute to PM10 levels, mainly in the dry season. Mineral dust concentrations (in TSP) during African dust outbreaks, frequently exceed 100$\mu g/m^3$ in the Canaries (Tegen and Ron, 1998; Tomza et al., 2001), 50$\mu g/m^3$ in the Cape Verde Islands (Chiapello et al., 1995), 20$\mu g/m^3$ in Barbados (Prospero and Ness, 1986; Savoie et al., 1992; Chiapello et al., 1995; Tegen and Ron, 1998) and 30$\mu g/m^3$ in Turkey (Kubilay et al., 2000; Tegen and Ron, 1998). Figure 2-1 shows an example of an African dust outbreak over the Canary Islands from February 26 to March 15 2000. During the African event, daily PM10 concentrations >100$\mu g/m^3$ were recorded over a long period, and up to 600$\mu g PM10/m^3$ were reached. The markedly reduced visibility provides direct evidence that the extremely high PM10 levels are caused by the high load of mineral dust.

Regional variations in the type of anthropogenic sources may also contribute to differences in PM10 chemical composition in Europe. Thus, the ratio $NO_3^-/SO_4^=$ is higher in Western than in Eastern Europe (Schaap et al., 2002). This is probably due to the use of different technologies, which results in higher NOx emissions in Western Europe and higher SO_2 emissions in Eastern Europe.

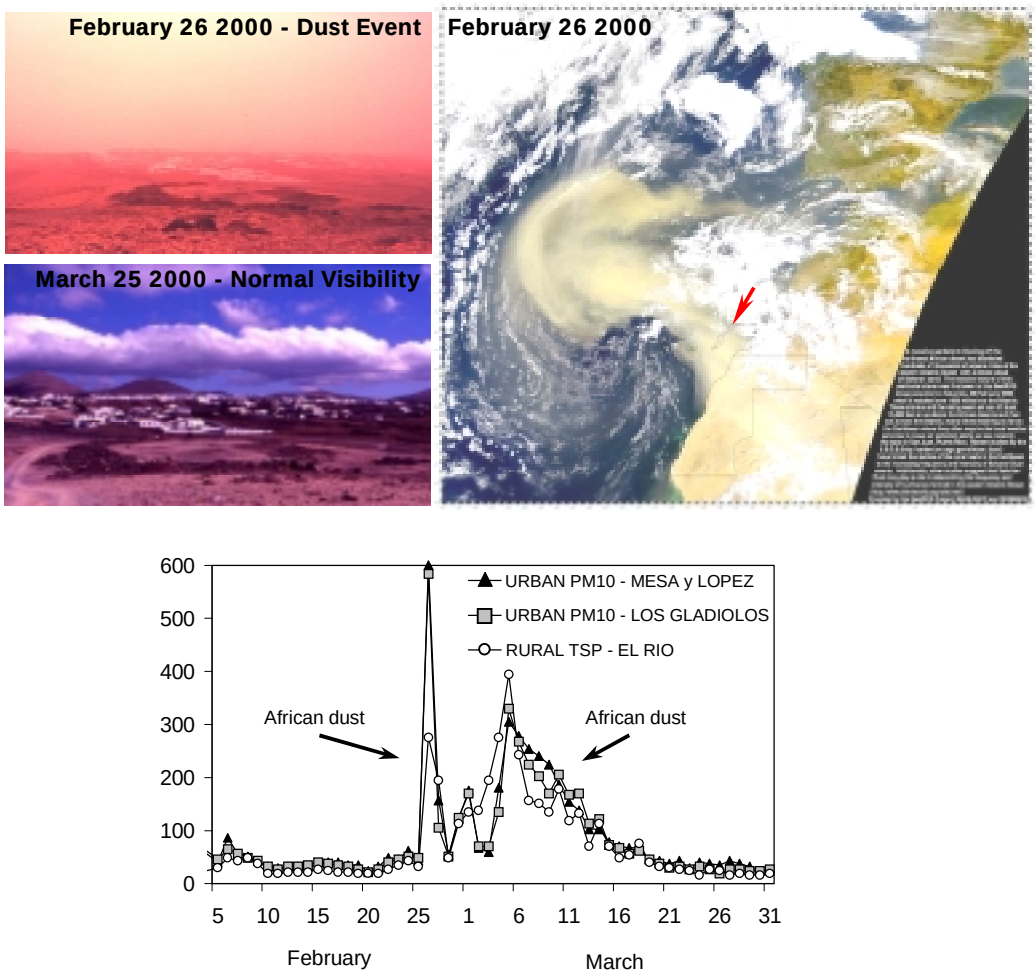

Figure 2-1. Upper left: Pictures taken at Lanzarote (Canaries) during and after an African dust event (Pictures taken by Mr. Jesus Yagüe). Upper right: SeaWIFS satellite image during the African dust outbreak over the Canary Islands (location highlighted with red arrow) in February 26 2000. Lower: daily PM10 and TSP levels recorded by the Canary Islands air quality monitoring network.

Figure 2-2. Map showing the orography and typical vegetal coverage in Europe.

Meteorology also plays an important role in differentiating between Southern and Central-Northern Europe. The latter regions are mostly characterised by a flat terrain, and are mainly affected by westerly winds, frequently associated with eastward moving depressions, cold fronts and rain. These factors favour dilution of pollutants, air mass renovation and pollutant scavenging. In contrast, the Western-Central Mediterranean is surrounded by high coastal ranges (Figure 2-2) and is frequently subject to weak baric gradient conditions. Under this scenario, the intense heating of semi-arid terrains promotes the breeze circulation and the development of meso-scale processes, favouring the ageing of pollutants by restraining the air mass renovation (Millán et al., 1996, 1997, 2000; Toll and Baldasano, 2000; Soriano et al., 1998, 2001; Gangoiti et al., 2001). Thus, the breeze circulation is typically associated with high surface ozone concentrations (Martín et al., 1991; Millán et al., 1997). This is attributed to re-circulations of polluted air masses over Eastern Spain. The lower frequency of Atlantic advections accounts for a lower scavenging potential and for the consequent longer residence time of suspended particulate matter in the atmosphere.

Studies performed by Millán et al. (1991, 1992, 1996, 1997, 2000) have shown that the high levels of ozone in Eastern Spain are favoured by the regional meteorology that encourages re-circulations of polluted air masses. These high surface ozone concentrations in Eastern Spain may also exert an influence on the secondary particle levels (Aires in ERAS, 2001) owing to the influence of photo-oxidant and reactive gases such as O_3, OH (formed by O_3 photolysis) or HO_2 (formed by OH oxidation) on the gas to particle conversion (e.g. sulphate, nitrate, or organic PM).

Thermodynamic properties exert an influence on gas - particle partitioning in the chemical components of low pressure vapour (such as ammonium-nitrate or some organic species; Wexler and Seinfeld, 1990; Raes et al., 2000). Thus, variations in the gas / particle distribution may also be different in Southern and Central-Northern Europe given that the Mediterranean is a warmer environment.

Some of these features have also been reported in earlier studies carried out on the development of suitable strategies for PM monitoring around large power stations in Eastern Spain (by Querol and co-workers). Around the Teruel power station (1050 MW) in the Ebro basin, Querol et al. (1998a, 1998b) found relatively high concentrations of crustal PM in PM10, and this was attributed to the re-suspension of the semi-arid soils and to the transport of African dust. Querol et al. (1999a) also reported very high SO_2 to $SO_4^=$ conversion rates, up to 6%/hour.

In a comparative study on PM10 levels in Europe, Hoek et al. (1998) found that PM10 levels in rural and urban areas increased gradually from Northern to Southern Europe.

In addition to these variations in PM features, the parameter used for PM monitoring is a key factor in assessing the air quality. Figure 2-3 shows an idealised size distribution of PM, where the conventional distinction between “fine” and “coarse” particles is indicated. As stated in chapter 1, fine particles (considered in the air quality context as those <2.5µm) are mainly

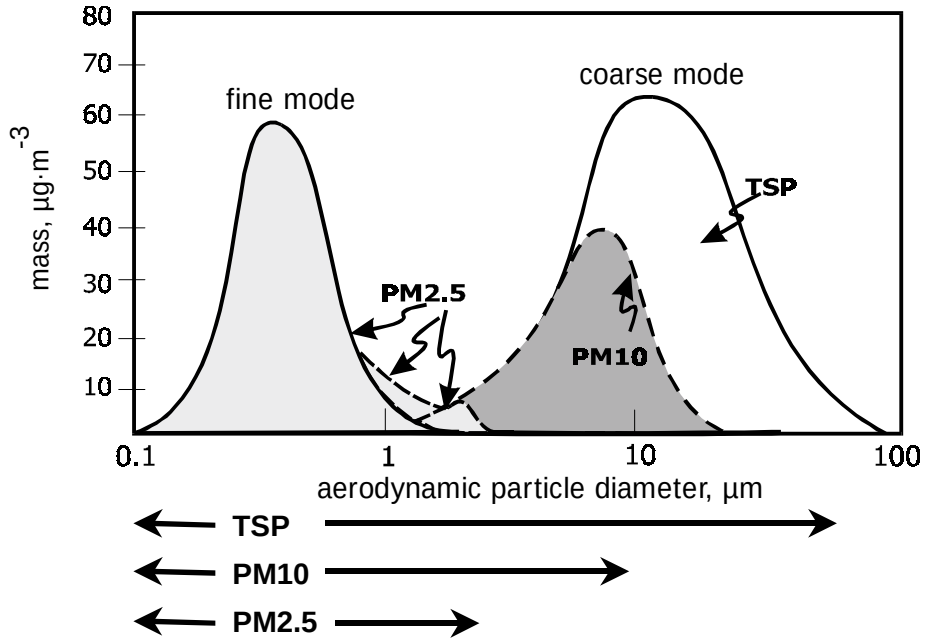

Figure 2-3. Ideal size distribution of particulate mass (US EPA, 1996).

anthropogenic and most of them are formed by gas to particle conversion processes (e.g. ammonium-sulphate or ammonium-nitrate). The most important exception is soot (or elemental carbon) which is primary. Coarse particles (2.5-10µm) are mainly formed by mechanical processes, and a significant fraction are natural (e.g. mineral dust and sea-spray). The most important exception is a fraction of nitrate and organic and elemental carbon in the coarse mode. Thus, PM2.5 is mainly constituted by anthropogenic particles, whereas PM10 includes a significant amount of natural PM in the range 2.5-10µm. The load of natural particles is even higher in TSP than in PM10, whereas PM1 is mainly constituted by anthropogenic PM. Thus, in regions with relatively high levels of natural crustal PM, the monitoring of PM2.5 instead of PM10 may avoid the influence of natural PM. However, PM2.5 is not a suitable parameter for monitoring PM levels in areas affected by primary PM emissions (e.g. manufacture of cement, ceramics or bricks).

Studies on PM characterisation in Europe have been mainly performed in Central and Northern Europe (e.g. Hoek et al., 1997; Krivacsy et al., 2001; Schaap et al., 2002) such as the United Kingdom (QUARC, 1996; Harrison et al., 1997a, 1997b, 2001; APEG, 1999; Turnbull and Harrison, 2000; Stedman et al., 2001), Germany (Lenschow et al., 2001), Switzerland (Monn et al., 1995; Röösli et al., 2001), Holland (Janssen et al., 1997; Zee et al., 1998; Wal et al., 2000), Norway (Pakkanen et al., 2000) or Finland (Pakkanen et al., 1996, 2001a, b, c). A significant number of studies have also been carried out in Portugal (Pio et al., 1991, 1996, 1998; Pio and Lopes, 1998; Harrison et al., 1997a). However, there are very few studies on PM characterisation in the Mediterranean basin (mainly Spain, Italy and Greece). Some TSP chemical characterisations are available from urban sites in Northern Italy (Caruso et al.,1981;

Annegarn et al.,1992; Braga Marcazzan,1996), and recently a PM10 and PM2.5 source apportionment has been performed in Milan (Marcazzan et al., 2001). Some studies have been undertaken in Spain, focusing on sulphate and trace metals in Valladolid (Sánchez and Ramos, 1987), on sulphate aerosol around the Teruel power station (Querol et al., 1998a, b, 1999a, b), on trace metals in urban TSP in Cartagena (Moreno-Grau et al., 2000) and Seville (Fernandez et al., 2000, 2001), and on the relationship between PM features and effects on Spanish monuments (Esbert et al., 2000). Although these PM chemical characterisations obtained from disparate studies are available, there are no studies on the behaviour of PM on a regional scale, in rural, urban and industrial environments.

2.2 Objectives of this study

This study is focused on the characterisation of PM in Eastern Spain from a multidisciplinary point of view. The influence of meteorology on PM levels, the physical and chemical characterisations of PM, and the PM source apportionment in different types of environments are addressed in this study. The specific aims of this study are as follows:

1. Determination of the range of TSP and PM10 concentrations in urban, industrial and rural environments in Eastern Spain, and evaluation of the degree of compliance of the EU standard for PM10.

2. Assessment of the influence of the meteorological processes on the PM10 levels in urban, industrial and rural sites in Eastern Spain. The contribution of the local and regional PM sources as well as that of long range transport of PM from North Africa and mainland Europe is evaluated.

3. Performance of a PM10 source apportionment study in rural, urban and industrial environments, and a simultaneous PM2.5 source apportionment study at an urban site in an attempt to assess the contribution of natural versus anthropogenic sources.

4. Evaluation of the degree of influence of the natural and anthropogenic particles on the parameters conventionally used for PM pollution monitoring, with a special emphasis on PM10 and PM2.5. This could play a role in the development of suitable strategies for PM monitoring in different environments and in the reduction of the interference of natural PM.

Some of these points have been discussed in studies performed in other regions. In Canada, PM10 levels at urban sites are 4-8 times higher than those at rural background sites (Environment Canada, 1997). By means of source apportionment studies, Kemerdere et al. (1997) found that the high regional PM10 levels (150µg/m^3 as PM10 mean value) in NE Turkey were caused by lignite-coal combustion, which accounted for 64% of bulk PM10. In the United States, crustal PM accounts for 36% and 19% of bulk PM10 in Western and Eastern US, respectively (US EPA, 1996). In Bullhead city (Arizona, US), Gertler et al. (1995) found that 79% of PM10 was caused by fugitive emissions of crustal PM, 16% of PM10 was caused by vehicle emissions, 4% of PM10 was made up of secondary-sulphate and <1% was made up of ammonium-nitrate. High contributions of crustal PM to ambient PM10 concentrations have also

been found in Mexico city (Chow et al., 2002). In Taiwan city, Chen et al. (1997) found that road traffic and bio-mass burning from agriculture were the most important sources of PM10 and PM2.5. King and Dorling (1997) and Stedman (1997a, 1997b, 1998) have associated the high PM10 episodes (>50µgPM10/m^3) with long range transport of secondary PM from Central and Eastern Europe.

Abatement strategies may significantly improve the air quality after identifying the main PM sources. Thus, the authorities in Britain took measures to reduce domestic and industrial smoke emissions (mainly from coal combustion) as a result of the smog episodes in the first half of XX century. Sulphate concentrations in London reached a maximum of 12µg/m^3 during the 70s, falling to 6µg/m^3 in the late 90s (APEG, 1999). This decreasing trend of sulphate levels contrasts with the increasing trend of nitrate: 1,5µg/m^3 in 1954 and 5µg/m^3 during the 90s. This contrasting trends of sulphate and nitrate are caused by the change in the use of technology and fuels.

2.3 Structure of this study

This study is made up of six chapters:

Chapter 1 - Introduction. The main characteristics and sources of atmospheric PM are summarised. The main environmental impacts of PM are discussed with an emphasis on the impact of PM on health and air quality.

Chapter 2 – Objectives of this study. The main factors which differentiate between Southern and Central-North Europe in terms of air pollution, meteorology and PM monitoring are discussed with special reference to the new EU standards for PM10.

Chapter 3 – Methodology. The ways in which PM data are obtained and interpreted are presented.

Chapter 4 – PM Events and seasonal evolution. The main meteorological processes affecting temporal variations of PM concentrations are identified and discussed on the basis of meteorological analysis, satellite observations and correlation with gaseous pollutants. Finally, the extent to which these events affect the PM seasonal evolution is assessed.

Chapter 5 – Chemical characterisation and source apportionment of PM10 and PM2.5. Receptor modelling techniques are used to identify PM10 and PM2.5 sources. The main processes affecting the temporal variations of the main PM chemical components are discussed. Finally, a PM10 source apportionment study is performed on a daily basis in rural, urban and industrial environments. A PM2.5 source apportionment study is also performed at the urban site.

Chapter 6 – Study of parameters for PM monitoring in ambient air. A set of PM10 and PM2.5 and cascade impactor samples, and grain size distribution measurements performed in a rural area affected by SO_2 emissions, at an urban site and in a specific industrial area affected

by primary PM emissions are presented and discussed. Conclusions on the suitable strategies for monitoring the anthropogenic load of PM in the different environments are drawn.