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Partitioning of major and trace components in PM_{10}–$PM_{2.5}$–PM_1 at an urban site in Southern Europe

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Abstract

Partitioning of major and trace components in PM_{10}–$PM_{2.5}$–PM_1 at an urban site in Barcelona (Spain) in the Western Mediterranean was studied in the period 2005–2006. Particular attention was paid to the partitioning of mineral matter and to the evidence of possible interactions of mineral matter with other pollutants (gaseous pollutants and secondary PM). The results showed a high contribution of mineral matter (mainly anthropogenic, but sporadically associated with African dust outbreaks) in levels of both PM_{10} and $PM_{2.5}$. A high proportion of nitrate was also present in the coarse fractions as a result of the interaction of mineral matter with gaseous pollutants. As at most urban sites in Europe, sulphate and carbonaceous aerosols are mainly present in the finer PM fractions. The $PM_{1-2.5}$ fraction resembled that of PM_{10} in composition. The chemically unaccounted fraction (mostly bounded water) had also a fine grain size, probably because of the fine size of the hygroscopic aerosol components. The data series follow an increasing trend for PM_1 levels (and less clearly for $PM_{2.5}$) from 1999 to 2006, whereas no trend is observed for PM_{10}.

The contributions of African dust and regional soil resuspension to the annual PM_{10} levels has been estimated in around 1–2 and 2–3 $\mu g\,m^{-3}$ in this part of Spain. The African dust outbreaks accounted for around 15–20 exceedances of the European daily PM_{10} limit value.

Finally, the data obtained were compared with data from selected European sites to highlight major differences in levels and speciation of PM.

Keywords: Atmospheric particulate matter; Speciation; Urban; Pollution; Mineral dust; Saharan dust

1. Introduction

Atmospheric particles are emitted from a wide variety of anthropogenic and natural sources, and consequently their physical and chemical properties may vary widely. In accordance with the atmospheric sciences, the fine PM mode includes particles $<1\,\mu m$ (PM_1; Whitby, 1978; Wilson and Suh, 1997). This is due to the fact that most particles in the coarse fraction ($>1\,\mu m$) are primary and generated by mechanical processes (such as mineral dust and sea spray). Coarse secondary particles may also be found (Wakamatsu et al., 1996; Querol et al., 1998), due to chemical interaction of gases with primary particles of crustal or marine origin (most $>1\,\mu m$). In the fine fraction (PM_1) particles may be primary (such as diesel soot), or secondary formed from

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gaseous precursors by nucleation or by condensation on existing particles.

According to health experts, the PM fraction $<100\,\mu m$ (PM_{100}) is known as inhalable PM. The PM fraction $<10\,\mu m$ (PM_{10}) is known as the thoracic fraction since it is able to enter the thoracic airways. Finally, there is a finer size fraction ($PM<4\,\mu m$ or PM_4) that could penetrate the conductive airways of the tracheobronchial tree that distributes the inhaled air to the gas-exchange airways in the lungs. This fraction is known as respirable PM (US-NIOSH—National Institute for Occupational Safety and Health, Centres for Disease Control and Prevention-guidelines). However, in air quality PM_{10} and $PM_{2.5}$ ($PM<2.5\,\mu m$ or alveolar fraction) are usually selected as monitoring parameters in worldwide environmental standards. Thus, in air quality, the coarse fraction is considered the one between 2.5 and $10\,\mu m$ ($PM_{2.5-10}$), whereas $PM_{2.5}$ is considered the fine fraction. This particular size discrimination is due to the fact that fine and coarse particles generally have distinct sources and formation mechanisms. However, as stated above, for the atmospheric scientific community these PM size ranges are not related to the formation mechanism. US-EPA (2004) states: 'Over the years, the terms fine and coarse, as applied to particles, have lost the precise meaning given in Whitby's (1978) definition. In any given article, therefore, the meaning of fine and coarse, unless defined, must be inferred from the author's usage.... Fine particles and $PM_{2.5}$ are not equivalent terms.'

In addition to the local and regional anthropogenic PM emissions, both the levels and composition of ambient air PM depend on climatology (mainly temperature, humidity, photochemistry, resuspension of soil particles, rain scavenging potential, re-circulation of air masses, dispersive atmospheric conditions) and on the geography (mainly proximity to the coast, topography, soil cover and proximity to arid zones) of a given region. Therefore, wide variations in PM levels and characteristics may be expected when considering different European regions such as the Southern Mediterranean, Eastern European or Scandinavian countries with very different climatologic and geographical patterns. Diverse environmental conditions and PM source characteristics may condition size partitioning of the PM components. Thus, a high load of PM mineral matter in dry regions of the EU may favour interaction with gaseous pollutants and give rise to a high proportion of coarse secondary PM (Harrison and Pio, 1983) when compared with wet and cold regions. Likewise, warm conditions may favour the partitioning of atmospheric pollutants towards the gaseous phases, which in turn may also interact with the coarse components and increase the secondary coarse PM load (Harrison and Kito, 1990; Wakamatsu et al., 1996).

This study focuses on the chemical speciation of PM_{10}, $PM_{2.5}$ and PM_1 during a 1-year period (October 2005–October 2006) at an urban site in Barcelona (North-eastern Spain), with special emphasis on mineral matter in order to better understand: (a) the mean partitioning of major and trace PM components, (b) the seasonal variations and (c) their source origin. Furthermore, PM_{10} and $PM_{2.5}$ 1999–2006 data and other PM data from prior studies carried out in Barcelona are also considered to support interpretations.

Data on levels and speciation of PM_1 in Europe are very scarce, especially in Southern Europe. Pakkanen et al. (2003) furnished data on PM_1 samples in Helsinki; Spindler et al. (2004, 2006) in a rural area of Germany; and Putaud et al. (2002), Vecchi et al. (2004), Giugliano et al. (2005) and Ariola et al. (2006) in different sites of Italy. The results of the partitioning of PM components in the <1, 1–2.5, and $2.5–10\,\mu m$ fractions in the study area (highly dust polluted) may help to yield further insight into the influence of mineral matter on the different PM grain size fractions, and to provide evidence of possible interactions of mineral matter with other pollutants (gaseous pollutants and secondary PM pollutants).

2. Methodology

2.1. Sampling and measurements

The PM monitoring site in Barcelona (North-eastern Spain) selected for this study is an urban background station (Barcelona-CSIC) exposed to road traffic emissions from the Diagonal Avenue (approximately 150 m distance), one of the largest avenues in the city. The monitoring station is located on the roof (two storeys) of the Institute of Earth Sciences "Jaume Almera". The levels of PM_{10}, $PM_{2.5}$ and PM_1 were measured continuously by means of a laser-spectrometer dust monitor (Grimm Labortechnik GmbH & Co. KG; models 1107 and 1108). Twenty-four hour samples of PM_{10}, $PM_{2.5}$ and PM_1 were simultaneously collected on quartz micro-fibre filters (Schleicher and Schuell;

QF20) by means of high-volume samplers equipped with PM_{10}, $PM_{2.5}$ and PM_1 inlets (DIGITEL; $30\,m^3\,h^{-1}$). Sampling was carried out at a rate of two samples of each PM fraction per week. Owing to technical problems, only 85 samples of each fraction were simultaneously sampled throughout the 10/10/2005–06/10/2006 period. The gravimetric data obtained were used to correct the PM_{10}, $PM_{2.5}$ and PM_1 measurements obtained with the laser spectrometer. Furthermore, 229 and 256 daily samples of PM_{10} and $PM_{2.5}$ were collected using the same procedure at the same sampling site from 27/03/2003 to 06/10/2006.

PM mass concentrations were determined by standard gravimetric procedures. Thereafter, 1/2 of each filter was acid digested ($HF:HNO_3:HClO_4$, with a mixture of 5:2.5:2.5 ml, kept at 90 °C in a Teflon reactor during 6 h, driven to dryness and re-dissolved with 2.5 ml HNO_3 to make up a volume of 50 ml with water) for the determination of major and trace elements by inductively coupled plasma atomic emission spectrometry and mass spectrometry (ICP-AES and ICP-MS, respectively). Another 1/4 of each filter was water leached to determine soluble ion concentrations by ion chromatography (sulphate, nitrate and chloride) and ion selective electrode (ammonium). The remaining 1/4 of each filter was used for the elemental analysis of total carbon (TC) by elemental analysers. Details of the analytical procedure are given by Querol et al. (2001). A selection of samples were analysed for organic and elemental carbon (OC and EC) by a thermal–optical transmission technique (Birch and Cary, 1996) using a Sunset Laboratory OCEC Analyser with the standard temperature programme. TC was determined as the sum of OC + EC + CC (being the late carbonate carbon). Moreover, SiO_2 and CO_3^{2-} were indirectly determined on the basis of empirical factors ($Al \times 1.89 = Al_2O_3$, $3 \times Al_2O_3 = SiO_2$ and $1.5 \times Ca = CO_3^{2-}$, mass ratios; see Querol et al., 2001). Organic and elemental carbon (OC + EC) were determined by subtracting mineral carbon (C in carbonates determined as above from Ca) from TC. The addition of the above determinations accounted for 75–85% of the PM_{10}, $PM_{2.5}$ and PM_1 mass. The remaining undetermined mass is attributed to the structural and adsorbed water that was not removed during the sample conditioning.

The chemical components of the PM were grouped as (a) crustal or mineral (sum of Al_2O_3, SiO_2, CO_3^{2-}, Ca, Fe, K, Mg, Mn, Ti and P); (b) marine component (sum of Cl^- and Na^+); (c) organic matter and elemental carbon, OM + EC (OM obtained applying a 1.6 factor to the OC concentrations); and (d) secondary inorganic aerosols, SIA (sum of SO_4^{2-}, NO_3^- and NH_4^+). Relative analytical errors were estimated using small amounts (5 mg) of the NIST-1633b (fly ash) reference material loaded on a 1/2 quartz microfibre filters. These reached values $<10\%$ for most elements, with the exception of P and K ($<15\%$).

Results were compared with PM_{10} and $PM_{2.5}$ speciation data obtained for the 1999–2006 at other sites in Barcelona obtained by using the same methodology.

2.2. Detection of African dust outbreaks

The possible day-to-day influence of external PM contributions from African dust outbreaks over this region of Spain was investigated by means of air mass back-trajectory analysis using the Hysplit model (Draxler and Rolph, 2003) and the information supplied by NRL-NAAPs, SKIRON and BSC-DREAM dust maps, and satellite images provided by the NASA SeaWIFS project

3. Results and discussion

3.1. PM levels

The mean levels of PM_{10}, $PM_{2.5}$ and PM_1 for the October 2005–October 2006 period were 41, 28 and $20\,\mu g\,m^{-3}$, respectively, as measured by the laser spectrometer and corrected by comparison with gravimetric levels, with data coverage of 95% of the days. These levels were similar to those obtained in the period 2003–2006 at the same monitoring site (39–42, 25–29 and 18–21 $\mu g\,m^{-3}$ for PM_{10}, $PM_{2.5}$ and PM_1, respectively). The mean levels for the 85 samples (for each of the three PM fractions) obtained with the high volume samplers were 45, 29 and $19\,\mu g\,m^{-3}$. The slight differences may be due to the fact that high volume sampling was done only on weekdays, when traffic density is higher, whereas the real time measurements also covered weekends. This difference was also evidenced in the other studies carried out in the metropolitan area of Barcelona (Tables 1 and 2).

As shown in Fig. 1, although mean annual levels of PM_{10} do not follow a definite trend, those of $PM_{2.5}$ and PM_1 (especially PM_1) tend to increase from 1999 to 2006. It is not easy to attribute this

Table 1
Mean levels of PM_{10}, $PM_{2.5}$ and PM_1 and their major components ($\mu g\,m^{-3}$) registered at different sites of Barcelona between 1999 and 2006

	PM_{10}					$PM_{2.5}$						PM_1[g]
	Barcelona-CSIC		Sagrera 2001[c]	L'Hospitalet[d] 1999–2000	Est.Francia[f] 2003	Barcelona-CSIC		Sagrera		L'Hospitalet[d] 1999–2000	Est.Francia[f] 2003	Barcelona-CSIC 2005–2006
	2003–2006[a]	2004[b]				2003–2006[a]	2004[b]	2001[c]	2001[e]			
N	274	32	90	115	72	300	31	44		63	72	108
PM	47	32	46	50	46	31	21	28	22	34	20	19
OC	5.7	ND	ND	7.7	4.8	5.3	5.1	ND	ND	ND	3.0	4.7
EC	2.2	ND	ND	3.3	1.9	2.3	2.2	ND	ND	ND	1.5	1.9
OC/(OC+EC)	0.72	ND	ND	0.70	0.72	0.70	0.70	ND	ND	ND	0.67	0.71
OC+EC	7.9	7.3	9.4	11.0	6.7	7.6	7.3	10.1	ND	11.0	4.5	6.6
OM+EC	11.5	10.5	13.7	15.9	9.6	11.0	10.5	12.2	ND	13.2	6.3	9.5
SO_4^{2-}	5.5	4.1	5.2	6.9	5.4	4.5	3.9	4.2	3.9	5.6	4.8	2.9
NO_3^-	5.1	3.4	3.9	5.8	4.2	3.0	2.1	2.2	ND	4.0	1.4	1.7
NH_4^+	1.8	1.8	2.0	3.2	1.7	1.8	1.8	2.0	ND	3.2	1.6	1.1
SIA	12.4	9.3	11.1	15.9	11.3	9.3	7.7	8.4	ND	12.8	7.8	5.8
Crustal	14.5	8.8	15.2	12.9	10.8	5.1	1.8	4.2	2.1	3.8	1.3	0.9
Sea spray	1.9	1.8	2.4	2.3	6.5	0.7	0.4	0.7	ND	0.8	1.2	0.2
Unaccounted	6.9	1.5	3.8	2.5	8.9	5.3	0.9	2.1	ND	4.2	3.4	3.2

ND, not determined and *N*, number of samples.

[a] Annual mean at Barcelona-CSIC 2003–2006 (Ph.D. Thesis of J. Pey and N. Pérez).

[b] Mean values for winter and summer measurement campaigns, by Viana et al. (2006, 2007).

[c] Annual mean, Querol et al. (2004).

[d] Annual mean, Querol et al. (2001) and Rodríguez et al. (2004).

[e] Annual mean, Götschi et al. (2005).

[f] Mean for a 2-month measurement campaign in spring (Sillanpää et al., 2005, 2006).

[g] Annual mean, this study.

Table 2
Mean levels of PM_{10}, $PM_{2.5}$ and PM_1 and their major components ($\mu g\,m^{-3}$) registered at Barcelona-CSIC from October 2005 to October 2006

	PM_{10}	$PM_{2.5}$	PM_1
N	85	85	85
PM	45	29	19
OC	5.6	5.5	4.3
EC	2.2	2.3	1.8
OC/(OC+EC)	0.72	0.70	0.71
OC+EC	7.8	7.8	6.1
OM+EC	11.3	11.3	8.7
SO_4^{2-}	5.2	4.6	3.3
NO_3^-	5.1	2.7	1.5
NH_4^+	1.4	1.4	1.2
SIA	11.7	8.6	2.7
Crustal	14.6	4.8	0.9
Sea spray	2.0	0.5	0.2
Unaccounted	6.4	5.3	3.4

N, number of samples.

upward trend exclusively to an increase in PM anthropogenic emissions given that data were obtained at different sites in Barcelona: (a) 1999–2000 at L'Hospitalet-Gornal, (b) 2001 at Sagrera, and (c) 2003–2006 at Barcelona-CSIC. Nevertheless, it should be noted that this trend is also observed for the 2003–2006 period when the measurements were carried out at the same site. In addition, the fact that the increasing trend is observed for the fine fractions but not for the coarser one suggests an anthropogenic origin. Thus, this increase could be related to the progressive rise in road traffic flow during the last decade (from 85,000 to 980,000 vehicles in 1999–2006 in the Barcelona city) and to the marked growth of the diesel fleet in Barcelona province (from around 26% in 1999 to around 43% in 2006, data from DGT, http://www.dgt.es/estadisticas/estadisticas03.htm and the Ajuntament de Barcelona, http://www.bcn.es/estadistica/catala/index.htm).

Diesel emits not only primary carbon (mainly EC according to literature) particles but also secondary organic aerosols. A recent paper (Robinson et al., 2007) has shown that photo-oxidation of diesel emissions rapidly generates organic aerosol, greatly exceeding the contribution from known secondary organic-aerosol precursors, probably due to the

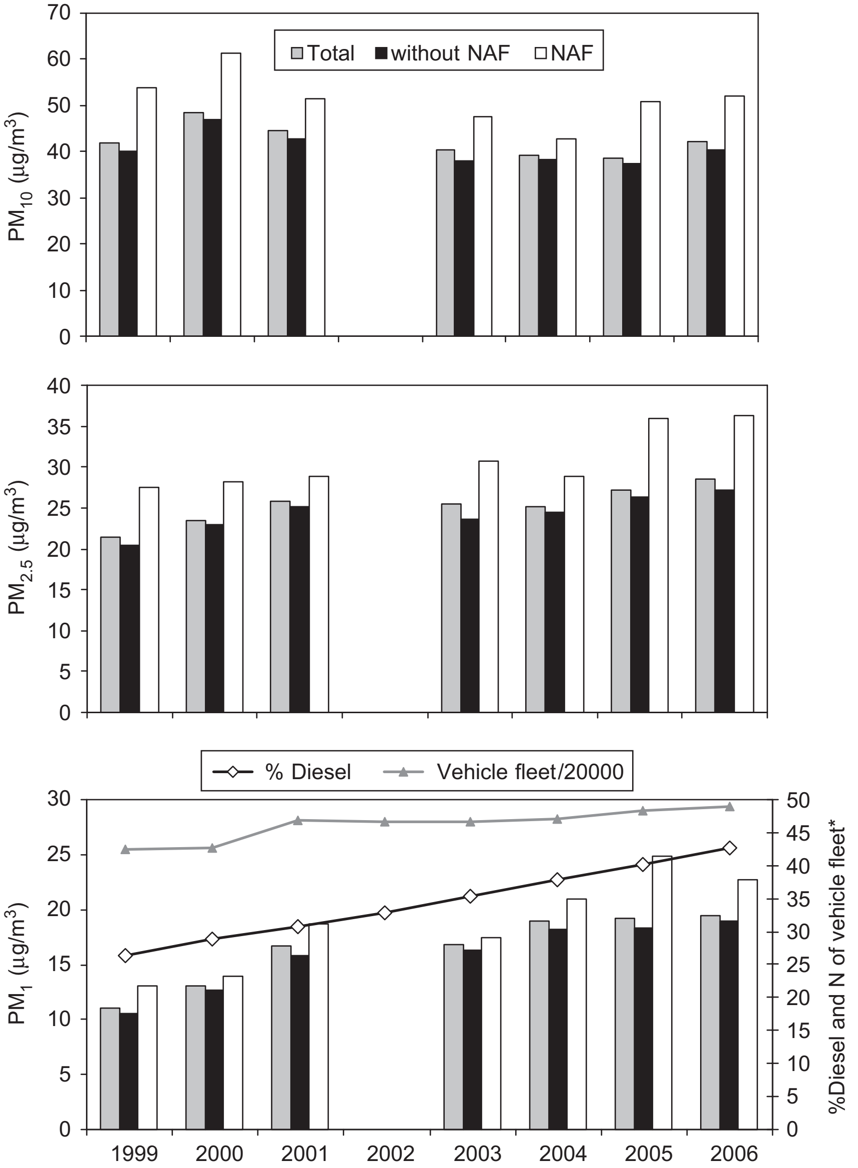

Fig. 1. Annual average levels of PM_{10}, $PM_{2.5}$ and PM_1 for the period 1999–2006 registered at different sites in the metropolitan area of Barcelona: 1999–2000, L'Hospitalet-Gornal; 2001, Sagrera; 2003–2006, Barcelona-CSIC. Mean levels considering only days with influence of African episodes (NAF) and excluding the African days (without NAF) are also presented. The bottom graph also contains the 1999–2006 evolution of the % of the diesel vehicle fleet in Barcelona province (26% in 1999 to 43% in 2006, data from DGT, http://www.dgt.es/estadisticas/estadisticas03.htm), as well as the vehicle fleet in Barcelona city (*total number of vehicles applying a factor *1/20000), data from Ajuntament de Barcelona (http://www.bcn.es/estadistica/catala/index.htm).

oxidation of low volatility gas-phases species. This may account for the relatively high proportion of OC/TC measured at Barcelona (70–72%), even with a high diesel/gasoline cars rate.

PM levels did not exhibit a marked seasonal trend (Fig. 2) although slightly lower levels were recorded during August–October. However, this minimum is not usually observed when considering the measurements since 1999 in Barcelona.

As regards the ratios PM_1/PM_{10} and $PM_{2.5}/PM_{10}$ mean values of 0.5 and 0.7 were obtained for the study period. These ratios show a marked decreasing trend from 0.6 to 0.7 in winter (October–March) to 0.4 and 0.6 in summer (April–September)

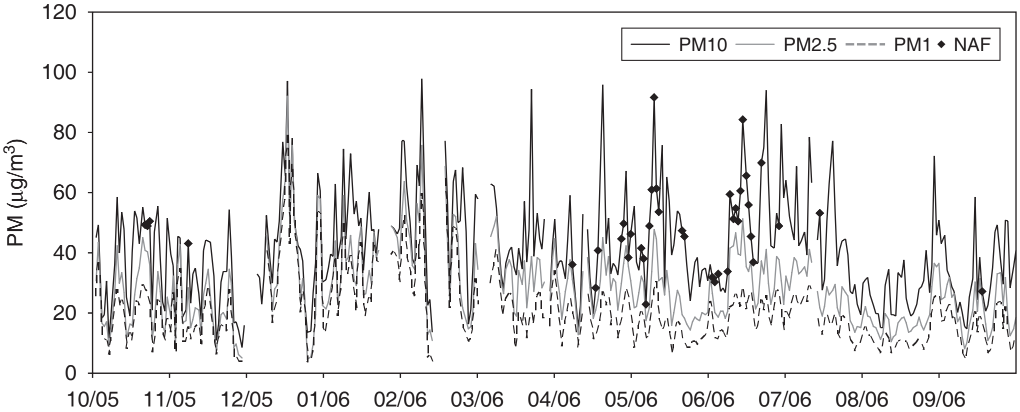

Fig. 2. Daily levels of PM_{10}, $PM_{2.5}$ and PM_1 recorded at the Barcelona-CSIC background site from 10/10/2005 to 6/10/2006. Days with African dust outbreak influence (NAF) are marked with black diamonds.

(Fig. 3). This decrease can be attributed to re-suspension, low precipitation and higher frequency of African dust episodes in summer (Querol et al., 2001; Viana et al., 2002; Escudero et al., 2005).

3.2. *Influence of African dust outbreaks and origin of the crustal load*

For the period considered (October 2005–October 2006), mean PM levels for days with African dust outbreaks reached 48, 33 and 20 $\mu g\,m^{-3}$ for PM_{10}, $PM_{2.5}$ and PM_1, respectively, and for the rest of the days 41, 28 and 20 $\mu g\,m^{-3}$. The PM_1/PM_{10} ratio decreased from 0.48 (mean annual average) to 0.42 for days with African dust influence. The $PM_{2.5}/PM_{10}$ ratio was similar in both cases (0.68–0.67). Thus, it is evident that PM_1 is less affected by African dust outbreaks than PM_{10} and $PM_{2.5}$.

The annual increase due to the African dust influence was 0.6–2.3, 0.5–1.4 and 0.1–0.6 $\mu g\,m^{-3}$ (1.6, 1.0 and 0.4 mean values, respectively) for PM_{10}, $PM_{2.5}$ and PM_1 during 1999–2006, as deduced from the difference between the annual PM levels and the mean values obtained for days without African dust influence. The wide range of values is probably due to the difference in frequency and intensity of African dust episodes (32 days in 2005 to 85 in 2003, with a mean value of 52 days $year^{-1}$).

The African dust crustal contribution to PM was also calculated as the difference between the crustal load averages determined by chemical speciation for the annual period and for the days without African dust influence. In the period 1999–2006, the African contribution to the crustal fraction was between 0.3–2.0 and 0.1–0.7 $\mu g\,m^{-3}$ for PM_{10} and $PM_{2.5}$ (3–14 and 2–14% of the mean annual crustal load in the two fractions), respectively. These African mineral dust contributions are similar to the mass contribution deduced from the mass balance of the bulk PM mass.

The influence of dust outbreaks is on average more relevant for the daily than the annual PM means. Daily African dust contributions to $PM_{10} > 25\,\mu g\,m^{-3}$ (up to 60) are usually reached a few days every year. Thus, from the 97 annual exceedances of the daily value from the European Air Quality Directive 1999/30/CE ($50\,\mu g\,PM_{10}\,m^{-3}$), 16 were attributed to African dust outbreaks (40% of the days with influence of African dust exceeded this value), whereas 81 (25% of days without African dust influence) were attributed exclusively to anthropogenic causes. Similarly, the $35\,\mu g\,PM_{2.5}\,m^{-3}$ daily value was exceeded during 18 days with African dust outbreaks (45% of the days with influence of African dust), whereas 71 (22% of days without African dust influence) were exclusively anthropogenic. For the period 1999–2006, the annual daily exceedances were between 63–104 for PM_{10} and 23–97 for $PM_{2.5}$. Of these days, between 10–30 (16–45%) for PM_{10} and 3–27 (13–65%) for $PM_{2.5}$ were recorded during days with African dust influence. Between 36–77 (55–84%) of the daily exceedances for PM_{10} and 9–70 (35–87%) for $PM_{2.5}$ were due exclusively to anthropogenic activity.

The origin of the crustal load in Barcelona-CSIC can be deduced by comparing the mineral contributions measured at the urban site and at Montseny, a

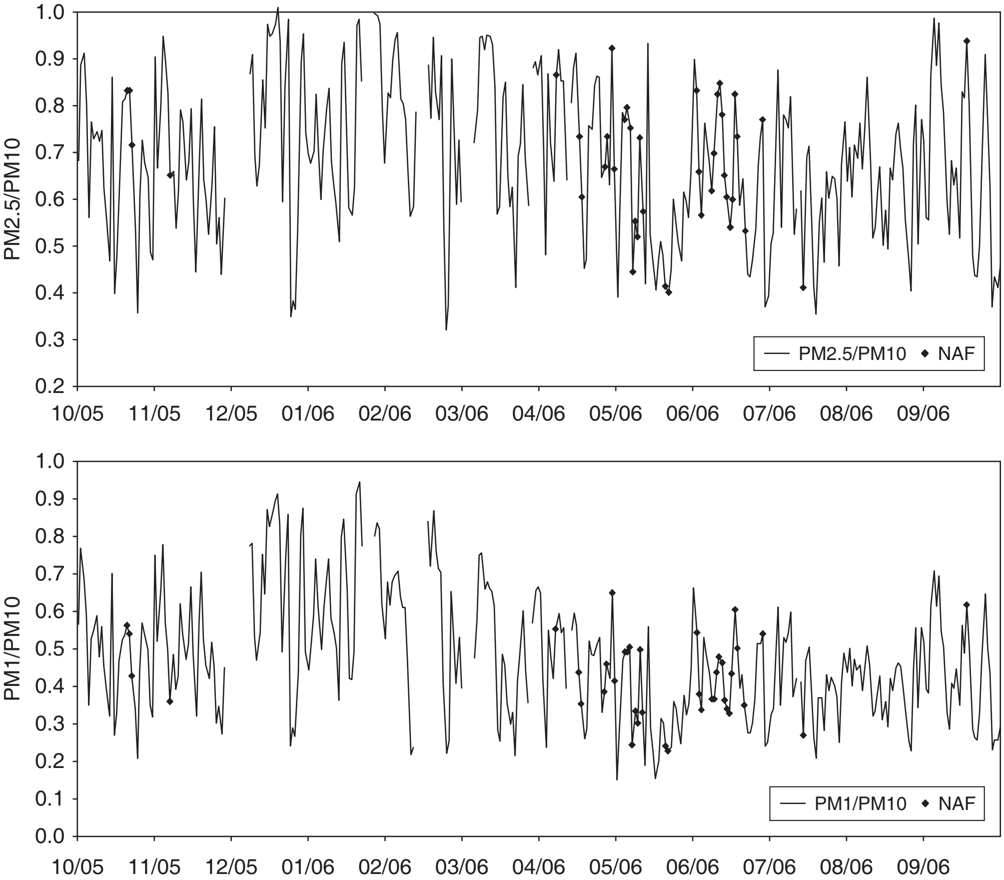

Fig. 3. Daily ratios $PM_{2.5}/PM_{10}$ (top) and PM_1/PM_{10} recorded at the Barcelona-CSIC background site from 10/10/2005 to 6/10/2006. Black diamonds (NAF) indicate the days with African dust outbreaks.

regional background site, 40 km to the north–east of Barcelona. The regional crustal load in Montseny can be broken down into regional soil re-suspension and African dust contributions (unpublished data by N. Pérez and J. Pey). The African dust contribution is obtained as the difference between the crustal annual mean for all the days and for the days without African dust influence. The mean crustal load for days without African dust outbreaks represents the regional soil contribution. Finally, if the regional mineral load at Montseny is subtracted from the bulk crustal levels in Barcelona, the urban mineral increment may be obtained. Results (Fig. 4) show that in the urban area of Barcelona the African dust, the regional soil re-suspension and the urban increment contributions to the annual mineral load in PM_{10} mean account for about 10, 20 and 70–75%, respectively. Similar relative values are obtained for $PM_{2.5}$ in spite of the different absolute concentration values. As a conclusion, at least 70–75% of the mineral dust load in both PM_{10} and $PM_{2.5}$ measured at the urban background site in Barcelona is anthropogenic.

4. Speciation of PM fractions $PM_{2.5–10}$, $PM_{1–2.5}$ and PM_1

Speciation data from simultaneous PM_{10}, $PM_{2.5}$ and PM_1 samples are presented in Table 2 and Fig. 5. The comparison with PM_{10} and $PM_{2.5}$ data from prior studies (Table 1) showed significant differences only for the crustal load, which varied greatly with time and space. Bearing this in mind, the partitioning of PM components in the $PM_{2.5–10}$ $PM_{1–2.5}$ and PM_1 fractions is described below using the simultaneously obtained data on PM_{10}, $PM_{2.5}$ and PM_1 during 2005–2006.

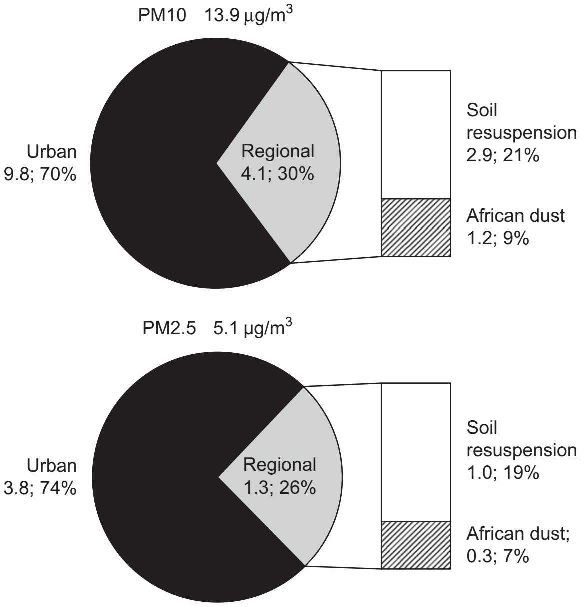

Fig. 4. Origin of the annual mean mineral contribution to PM_{10} and $PM_{2.5}$ at the Barcelona-CSIC site between 2004 and 2006. Data are given in $\mu g\,m^{-3}$ and %.

4.1. *Composition of the fractions PM_{10}, $PM_{2.5}$, $PM_{2.5-10}$ $PM_{1-2.5}$ and PM_1*

The coarse fraction ($PM_{2.5-10}$) was mainly made up of mineral dust (63%) and sea spray (10%) although proportions of coarse-SIA (Ca, K, Mg sulphates and Na and Ca nitrates) were also present (20–25%). The carbonaceous material was found at very low levels in this fraction.

Sea spray and mineral dust were reduced in $PM_{2.5}$ (2% and 16%, respectively) with respect to PM_{10} (5% and 32%, respectively). Most of the carbonaceous components present in PM_{10} also fall within the $PM_{2.5}$ range (almost no OM + EC is present in $PM_{2.5-10}$) but as stated above a fraction of the SIA, particularly nitrate, was coarse, and consequently not present in $PM_{2.5}$. Thus, $PM_{2.5}$ was still a mixture of SIA (30%), carbonaceous material (34%) and a large proportion of mineral dust (16%). The mineral load in $PM_{2.5}$ continues to be high given the influence of primary PM emissions at urban sites.

The mineral matter load in PM_1 (5%) was much more reduced than in $PM_{2.5}$ (16%). Around 80% of the carbonaceous material present in $PM_{2.5}$ continued to be found in PM_1. However, concentrations

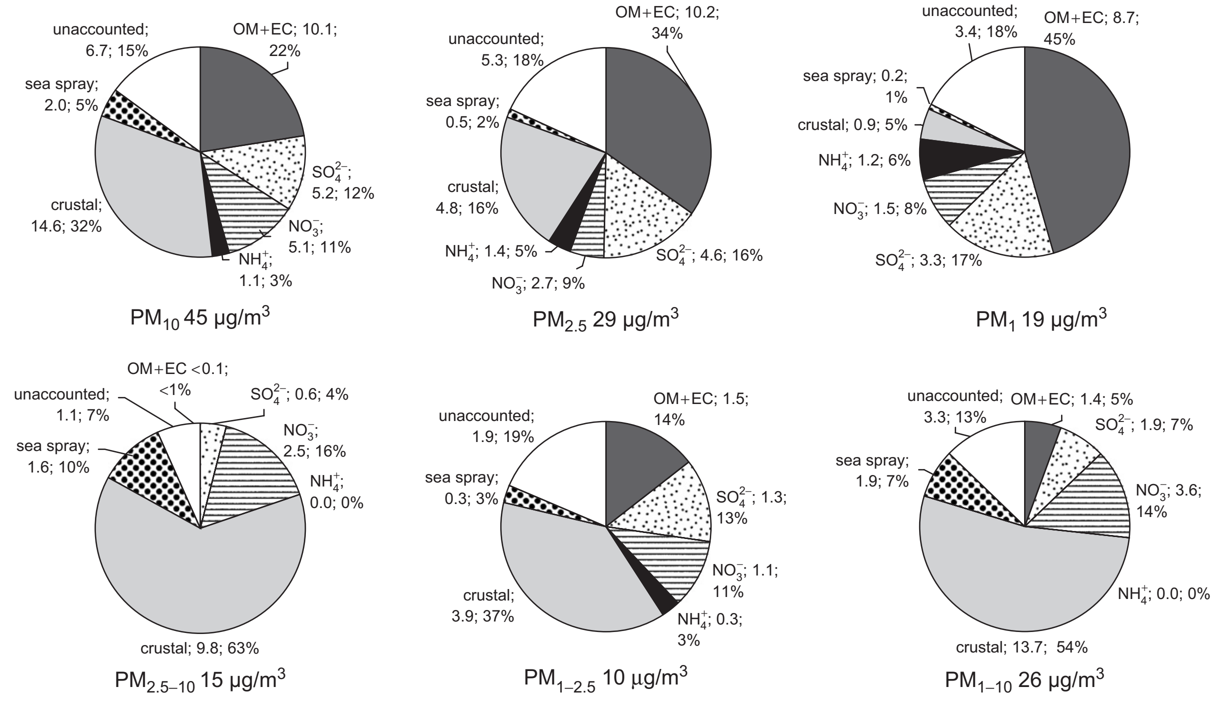

Fig. 5. Mean composition of PM_{10}, $PM_{2.5}$ and PM_1 at the Barcelona-CSIC site, from 10/10/2005 to 6/10/2006. Data are given in $\mu g\,m^{-3}$ and %. OC, organic carbon; EC, elemental carbon; and CC, carbonate carbon.

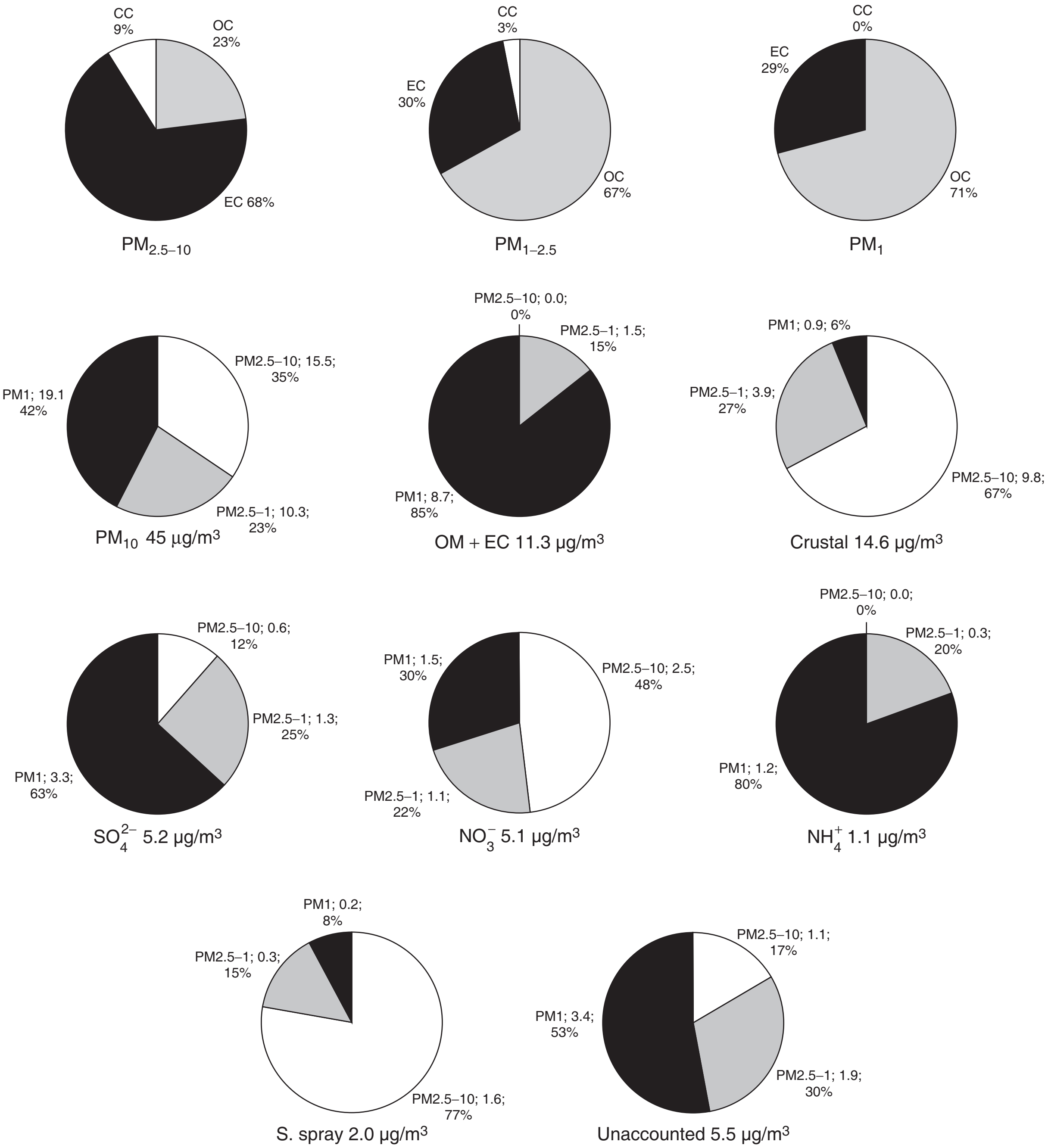

Fig. 5. (*Continued*)

of SIA (especially nitrate levels) were reduced by 20–30% in PM_1 with respect to $PM_{2.5}$. Thus, the $PM_{1–2.5}$ fraction was made up of mineral dust (37%) and SIA (27%), with a fraction of carbonaceous matter (14%). The PM_1 fraction was predominantly made up of OM + EC (45%), SIA (31%) and minor proportions of mineral dust and sea spray.

It is important to highlight that the composition of the PM_{10} and $PM_{1–2.5}$ fractions (Fig. 5) is very similar and this suggests that $PM_{2.5}$ still contains a high percentage of what it is generally considered as coarse fraction.

4.2. Partitioning of PM components in PM_1/$PM_{1–2.5}$/$PM_{2.5–10}$

The *crustal component* is mainly coarse, although it is still present in $PM_{2.5}$ in significant amounts (6/27/67% for PM_1/$PM_{1–2.5}$/$PM_{2.5–10}$). As stated above, the high mineral dust load arises mainly from anthropogenic emissions, such as road dust re-suspension, demolition and construction. Dust accumulation on roads is favoured by the relatively long periods without rain in this region. A lower contribution is attributed to African dust events and natural re-suspension from arid soils.

The *sea spray* is mainly coarse (8/15/77% for PM_1/$PM_{1–2.5}$/$PM_{2.5–10}$). A significant fraction is still present in $PM_{2.5,}$ but markedly diminished in PM_1.

Carbonaceous material (OM + EC) was mainly present in the fine fraction (85/15/<1% in the PM_1/$PM_{1–2.5}$/$PM_{2.5–10}$). In this urban environment, the carbonaceous material is mainly anthropogenic, emitted by road traffic and in a minor proportion by power stations, specific industrial processes, biomass combustion and biogenic emissions. Regarding EC, OC and CC partitioning, the percentages obtained were 29/30/68 for EC, 71/67/23 for OC and 0/3/9 for CC, in the PM_1/$PM_{1–2.5}$/$PM_{2.5–10}$ fractions, respectively. These data show that the OC/EC ratio is opposite in the $PM_{2.5–10}$ fraction compared with the $PM_{1–2.5}$ and PM_1 fractions. As expected, the contribution of CC was negligible in PM_1.

Sulphate was distributed among the three PM fractions with a fine grain size (63/25/12% in the PM_1/$PM_{1–2.5}$/$PM_{2.5–10}$) as a consequence of the prevalence of ammonium sulphate (fine aerosols) versus the coarser Ca, Na or Mg sulphate species.

Nitrate was distributed among the three PM fractions with a shift towards the coarse fraction (30/22/48% in PM_1/$PM_{1–2.5}$/$PM_{2.5–10}$). The slightly coarser size distribution is due to the prevalence of fine ammonium nitrate, but coarser Na and Ca nitrate also occur in appreciable levels.

Ammonium showed a fine size distribution (80/20% in the PM_1/$PM_{1–2.5}$) as a consequence of the fine grain size of ammonium sulphate and nitrate. Most of the ammonium present in PM_{10} also falls in the $PM_{2.5}$ range, on occasions with lower concentrations in PM_{10} than in $PM_{2.5}$ due to sampling artifacts (Querol et al., 2001).

The *unaccounted mass* followed a size distribution very similar to that reported for sulphate (53/30/17% in PM_1/$PM_{1–2.5}$/$PM_{2.5–10}$). These species are very hydrophilic and tend to accumulate water (the main cause of the unaccounted mass).

5. Trace elements

The mean levels of trace elements (including metals; Table 3) do not present a large time and spatial variation in the Barcelona metropolitan area, barring a few exceptions such as Zn (higher contents in L'Hospitalet) and Pb (higher contents before 2001 when unleaded petrol became obligatory). Other studies showed mean annual levels of up to 12 $\mathrm{ng\,m^{-3}}$ of As in $PM_{2.5}$ at Sagrera (Götschi et al., 2005) which may be considered as anomalously high with respect to the other studies, with annual means of As < 1 $\mathrm{ng\,m^{-3}}$. This difference may be ascribed to the analytical methodology. Götschi et al. (2005) determined As by X-ray fluorescence (XRF), whereas the other studies used ICP-MS.

The levels of trace elements did not exceed the limit and target values of the CE standards (2004/107/CE–1999/30/CE). However, the levels of V and Ni (mainly due to fuel oil combustion) and Mn, Ba, Cu, Zn, Sb and Li (mainly attributed to road dust) recorded in Barcelona are in the upper range of the concentrations registered at urban background sites with low industrial influence in Spain (Querol et al., 2008).

The trace elements showed a clear partitioning trend between the $PM_{1–10}$ and the PM_1 fraction, probably reflecting the origin of some of these elements. Elements associated with fossil fuel combustion (V, Ni) or other high temperature industrial processes (As, Cd, Pb and U) occur in very fine particles (50–82% in the PM_1 fraction). Other elements usually associated with mineral matter emitted by road dust, construction and/or demolition, such as Ti, Li, Rb, Sr, La, Ce, P and Th, or with road traffic abrasion products (mainly from tires and brakes) such as Sb, Cu, Mn, Cr, Co, Sn, Tl, Ba, Bi, Se and Zn (Wahlin et al., 2006; Schauer et al., 2006) tend to accumulate in the coarse mode (68–95% in the fraction $PM_{10–1}$).

6. Comparison of PM patterns with those from other European regions

6.1. PM levels

The PM levels measured in Barcelona (41, 28 and 20 $\mu\mathrm{g\,m^{-3}}$ for PM_{10}, $PM_{2.5}$ and PM_1, respectively

Table 3
Mean levels of trace elements (ng m^{-3}) in PM$_{10}$, PM$_{2.5}$ and PM$_1$ registered in different sites at Barcelona between 1999 and 2006

	PM$_{10}$			PM$_{2.5}$				PM$_1$[e]
	Barcelona-CSIC 2003–2006[a]	Sagrera 2001[b]	L'Hospitalet[c] 1999–2000	Barcelona-CSIC 2003–2006[a]	Sagrera		L'Hospitalet[c] 1999–2000	Barcelona-CSIC 2005–2006
					2001[b]	2001[d]		
Li	0.6	0.7	ND	0.3	0.2	ND	ND	0.1
P	30	32	44	14	19	ND	30	5
Ti	45	84	54	17	26	19	16	1.8
V	12	15	13	9	10	9	9	6
Cr	6	8	6	3	3	ND	6	1.2
Mn	20	23	24	10	10	10	14	4
Co	0.4	0.4	ND	0.2	0.3	ND	ND	0.1
Ni	6	7	7	4	5	ND	6	3
Cu	80	49	74	43	31	21	52	12
Zn	103	98	263	69	55	80	191	48
As	1.1	1.5	ND	0.8	1.0	12.5	ND	0.6
Se	0.9	1.1	ND	0.6	0.8	ND	ND	0.3
Rb	1.3	1.8	ND	0.5	0.7	ND	ND	0.2
Sr	6	6	7	2	2	ND	4	0.9
Cd	0.5	0.7	ND	0.4	0.6	ND	ND	0.3
Sn	6	4	ND	3	4	ND	ND	2
Sb	7	10	ND	3	4	ND	ND	0.9
Ba	27	41	38	12	9	ND	23	9
La	0.4	0.6	ND	0.2	0.2	ND	ND	0.1
Ce	0.9	1.3	ND	0.4	0.5	ND	ND	0.2
Tl	0.3	0.3	ND	0.2	0.3	ND	ND	0.1
Pb	26	58	149	19	40	53	130	17
Bi	0.6	0.4	ND	0.4	0.2	ND	ND	0.2
Th	0.1	0.3	ND	0.1	0.2	ND	ND	0.1
U	0.1	0.2	ND	0.1	0.3	ND	ND	0.1

ND: not determined.

[a] Annual mean levels, Querol et al. (2004, 2008) and Ph.D. Thesis of J. Pey and N. Pérez.

[b] Annual mean, Viana (2003) and Querol et al. (2004, 2008).

[c] Annual mean, Querol et al. (2001), Rodríguez (2002) and Rodríguez et al. (2003).

[d] Annual mean, Götschi et al. (2005).

[e] Annual mean, non-published data, Ph.D. Thesis N. Pérez.

for 2005–2006) may be considered as relatively high when compared with the average ranges observed at urban and industrial background sites in Spain, which reach values of 30–46 μg PM$_{10}$ m^{-3} and 20–30 μg PM$_{2.5}$ m^{-3} (Querol et al., 2008).

PM levels are relatively high in urban agglomerations in Southern Europe. High PM anthropogenic emissions in narrow streets, a warm and dry climate, low dispersive conditions, soil re-suspension and a sporadic contribution from Northern African dust could account for the high PM levels. Theses factors mainly affect the coarse fraction. Sillanpää et al. (2005) reported, for 2002–2003, PM$_{10}$ levels for Central and Northern EU cities ranging from 20 to 35 μg m^{-3}, and 46 to 54 μg m^{-3} from Barcelona (41–46 μg m^{-3} in the current study from continuous measurements with >90% data availability for 2003–2006) and Athens (54 μg m^{-3}). Conversely, PM$_{2.5}$ levels were higher in Prague and Amsterdam than in Barcelona, which indicates that the PM$_{2.5-10}$ fraction is markedly higher in Southern Europe. However, data from the current study shows also relatively high levels of PM$_{2.5}$ (25–28 μg m^{-3} from the above continuous measurements), exceeding the forthcoming EU standards (20 or 25 μg m^{-3}), compared with the usual concentration ranges measured in Northern (10–18 μg PM$_{2.5}$ m^{-3}) and Central (15–20 μg PM$_{2.5}$ m^{-3}, 30–40 μg PM$_{2.5}$ m^{-3} in specific areas with adverse meteorological conditions) Europe (EMEP, 2007).

Although PM$_1$ data are scarce in Europe, the levels measured in Barcelona (20 μg PM$_1$ m^{-3}) may be considered also relatively high when compared with available data (Table 4): from 11–12 μg m^{-3} in

Table 4
Mean levels ($\mu g\,m^{-3}$) of PM_1 and major components registered at some European sites between 1997 and 2006

	Milano[a]	Helsinki[b]	Melpitz[c]	Milano (rural)[d]	Barcelona-CSIC
N	105	4	153	NA	108
PM_1	29	11	12	20	19
OC	13.0	ND	ND	5.6	4.7
EC	1.9	ND	ND	ND	1.9
OM + EC	20.1	ND	3.6	ND	9.5
SO_4^{2-}	3.9	1.3	2.3	2.9	2.9
NO_3^-	ND	0.1	2.0	3.8	1.7
NH_4^+	1.5	0.6	1.4	2.2	1.1
Crustal	0.4	0.3	0.5	ND	0.9
Cl^-	0.2	<0.1	ND	ND	0.1

ND, not determined and NA, not available.
[a] Vecchi et al., 2004, Atmospheric Environment (data from 2002).
[b] Pakkanen et al., 2003, Atmospheric Environment (data from June 1997).
[c] Spindler et al., 2006 in EMEP (data from 2004–2006).
[d] Putaud et al., 2002 JGR (data from 2000–2001).

Helsinki (Pakkanen et al., 2003) and in rural areas of Germany (Spindler et al., 2004, 2006) to 29–34 $\mu g\,m^{-3}$ in Milan (Putaud et al., 2002; Vecchi et al., 2004).

6.2. *Mineral matter*

Except for the Scandinavian countries, where a high mineral load in PM_{10} is recorded as a consequence of road sanding and the use of studded tires in winter (Areskoug et al., 2004; Norman and Johansson, 2006), urban areas of the rest of Europe registered lower mineral loads in PM_{10} than those reported in Southern Europe (Querol et al., 2004). In $PM_{2.5}$ this differentiation is still patent. Rodríguez et al. (2007) determined for 2004 annual mean mineral loads in $PM_{2.5}$ of 0.8 $\mu g\,m^{-3}$ in London and of 4 $\mu g\,m^{-3}$ at a similar site in Barcelona (similar to the levels determined in the present study, 3.8–5.1 mean annual levels from 1999 to 2006). The higher mineral load in urban areas of Southern Europe compared with Central Europe is attributed to the lower precipitation. Rainfall favours not only the atmospheric scavenging of atmospheric pollutants but also the washout of road dust and the prevention of re-suspension. In PM_1, the mineral load is very reduced with respect to $PM_{2.5}$ and PM_{10}, and the geographical differences diminish in terms of absolute concentration levels. Thus, the mean annual mineral load in PM_1 measured in Barcelona reached 0.9 $\mu g\,m^{-3}$, which is much closer to the one reported for Milan (0.5–0.4 $\mu g\,m^{-3}$) by Vecchi et al. (2004).

6.3. *OC+EC*

Levels of OC + EC measured at the urban background site in Barcelona were in the range of levels recorded in most urban background areas in Europe (5–18 $\mu g\,m^{-3}$ mean annual levels in PM_{10} and $PM_{2.5}$ in central Europe and even lower in Scandinavian cities; Querol et al., 2004), with a fine grain size distribution (>80% in $PM_{2.5}$). Higher values have been measured in some Eastern European cities, with levels of up to 35–50 μg OC + EC m^{-3} in PM_{10} measured in short winter campaigns at different sites in Krakow (Putaud, 2006; Marelli et al., 2006). At urban sites, major sources of these compounds are traffic, coal, fuel oil and biomass combustion. Levels of these compounds will depend mainly on the proximity and emission rate of these sources in the area.

The OC/EC ratios measured in Barcelona by different studies, years and sites fall in a relatively narrow range 2.0–2.6 (70–72% of the non-mineral carbon being attributable to OC). These ratios are intermediate when compared with the values measured at kerbside sites (1.2–2.0; Viana et al., 2006) and at urban background sites (3.0–4.0; Lonati et al., 2007). This may be attributable not only to the high traffic influence, but also to the high proportion of diesel cars in Barcelona.

6.4. *SIA*

At most urban background sites in Europe, levels of SIA extend from 3 to 11 $\mu g\,m^{-3}$ for PM_{10} and

$PM_{2.5}$, with the lowest SIA concentrations being registered in Scandinavian cities. At some sites in Eastern Europe much higher concentrations have been measured. Thus, Putaud (2006) obtained concentrations of up to 15–20 μg SIA m^{-3} PM_{10} in very short winter campaigns at different sites in Krakow. In Barcelona, levels of SIA in PM_{10} were close to 11 $\mu g\, m^{-3}$. Spatial distribution of levels of sulphates is relatively homogenous, showing similar concentrations for regional and urban areas owing to their secondary origin and their fine distribution. Levels of nitrate are usually higher in urban or industrial areas than at regional background sites. This difference may be ascribed to the development of ammonium nitrate episodes in urban areas under specific scenarios (Drechsler et al., 2006).

6.5. *Sea spray*

Sea spray contribution to PM_{10} is fairly homogenous in mainland Europe with annual mean concentrations in $PM_{10} < 1$–$2\,\mu g\, m^{-3}$. At coastal sites, concentrations reported along the Mediterranean coast (2–4 $\mu g\, m^{-3}$; Querol et al., 2004) are clearly lower than those reported at the Atlantic coastal sites (up to 7 $\mu g\, m^{-3}$ in The Netherlands and Ireland; Visser et al., 2001; Finnan, 2006). The highest sea spray contributions have been measured in the Canary Islands, with annual concentrations of up to 11 $\mu g\, m^{-3}$ (Querol et al., 2004). In $PM_{2.5}$, this contribution is markedly reduced and the levels are <1–$2\,\mu g\, m^{-3}$ at most sites.

7. Conclusions

Comparing the PM levels recorded in this study with other European regions with different climatological and geographical patterns, it may be concluded that PM levels are relatively high at Barcelona. High PM anthropogenic emissions, narrow streets, together with a dry and warm Mediterranean climate, low dispersive conditions, soil re-suspension and sporadic contribution from North African dust could account for the high PM levels. This difference is more marked for the coarse fraction, but is also evident for sulphate.

Results of PM speciation and size partitioning obtained at an urban site in Barcelona (Spain) show that the coarse fraction ($PM_{2.5-10}$) mainly consists of mineral dust (63%), sea spray (10%), and secondary inorganic aerosols (mostly Na, Ca, K, Mg sulphate and nitrate, 20–25%). The $PM_{1-2.5}$ fraction is made up of mineral dust (37%) and secondary inorganic aerosols (27%), with a fraction of carbonaceous matter (14%). The PM_1 fraction mainly comprises OM + EC (45%) with an important fraction of secondary inorganic aerosols (mostly ammonium nitrate and sulphate, 31%) and very minor proportions of mineral dust and sea spray. Thus, PM_1 contains a significantly lower proportion of crustal and marine components and a larger proportion of carbonaceous components than the PM_{1-10} fraction. Levels of mineral dust in PM_1 are comparable to those recorded in other climatic regions of Europe.

The relatively high levels of mineral dust and the high proportion of coarse nitrate are PM patterns peculiar to Barcelona when compared with central and western European urban sites.

The results show that the strategy of combining PM_{10} and PM_1 monitoring is a good tool for air-quality monitoring across Europe. In PM_1, the dust load is considerably reduced when compared with PM_{10} and $PM_{2.5}$, and the measurement of PM_1 allows us to monitor levels of the same components (mostly carbonaceous and secondary inorganic components) in different European scenarios. Simultaneously measured PM_{10} could also provide information on the levels of specific coarse components for a given site, such as mineral dust and sea salt. $PM_{2.5}$ represents an intermediate stage, and may also be influenced by mineral dust. Thus, the composition of $PM_{2.5}$ varies across Europe more than PM_1.

The mineral contribution to the annual PM_{10} levels at the Barcelona study site can be broken down into an urban background fraction (65–70%) and a regional background fraction (30%). The regional crustal load can be broken down into the regional soil re-suspension (20–25%) and the African dust contribution (8–16%). Thus, most of the mineral load at this urban site has an anthropogenic origin.

The contribution of African dust to PM levels depends on the frequency and intensity of African dust episodes in a year. In Barcelona, for the period 1999–2006, between 16% and 45% of the exceedances of the daily limits for PM_{10} were recorded during African dust outbreaks episodes, but not in all cases were the exceedances exclusively caused by the natural contribution.

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