ATMOSPHERIC PARTICULATE MATTER IN SPAIN: LEVELS, COMPOSITION AND SOURCE ORIGIN

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ABSTRACT

Average ranges of PM_{10} and $PM_{2.5}$ concentrations and chemical composition in Spain show significant variations across the country, with current PM_{10} levels at several industrial and traffic hotspots exceeding recommended pollution limits. Such variations and exceedences are linked to patterns of anthropogenic and natural PM emissions, climate, and reactivity/stability of particulate species. PM_{10} and $PM_{2.5}$ concentrations reach 13-21μgPM_{10}/m^3 and 8-14μg$PM_{2.5}$/m^3 in EMEP type regional background sites, 19-21μgPM_{10}/m^3 and 12-17μg$PM_{2.5}$/m^3 in most rural sites, 28-32μgPM_{10}/m^3 and 18-25μg$PM_{2.5}$/m^3 in suburban sites, 28-47μgPM_{10}/m^3 and 19-29μg$PM_{2.5}$/m^3 in urban background and industrial sites, and 46-50μgPM_{10}/m^3 and 28-35μg$PM_{2.5}$/m^3 in heavy traffic hotpots. Spatial distributions show sulphate and carbon particle levels reaching maximum values in industrialised areas and large cities (where traffic emissions are higher), and nitrate levels increasing from the Atlantic to the Mediterranean coast (independently of the regional NO_x emissions). African dust outbreaks have an influence on the number of exceedances of the daily limit value, but their additional load on the mean annual PM_{10} levels is only highly significant in Southern Iberia and the Canary and Balearic islands. The marine aerosol contribution is near one order of magnitude higher in the Canaries compared to the other regions. Important temporal influences include PM intrusion events from Africa (more abundant in February-March and spring-summer), regional scale pollution episodes, and weekday *vs*. weekend activity. Higher summer insolation enhances $(NH_4)_2SO_4$ levels but depletes particulate NO_3^- (as a consequence of the thermal instability of ammonium nitrate in summer) and Cl^- (due to HCl volatilisation resulting from the interaction of gaseous HNO_3 with the marine NaCl), and it is also related to a general increase of dry dust resuspension under a semi-arid climate conditions. Average trace metal particle concentrations show the highest levels at industrial and traffic hotspots sites, sometimes exceeding rural background levels by over an order of magnitude (Ti, Cr, Mn, Cu, Zn, As, Sn, W and Pb). Levels of Cu and Sb are relatively high in urban areas when compared with industrialised regions. This is probably due to the fact that in urban areas important PM emissions arise from brake abrasion from road traffic. Cu, Sb, Fe and Zn are major constituents of brakes in vehicles. Levels of Cr, Mn, Ni, Zn, Mo, Se, Sn and Pb are higher in areas with steel production. Levels of As, Bi and Cu are relatively higher in areas with copper metallurgy industry. The levels of Zn are relatively high around zinc metallurgy hotspots. Levels of V and Ni are relatively high only in one of the areas with petrochemical plants, but probably have a low relationship with such plants and are likely to be emitted from fuel oil combustion. These conclusions may be also valid for other petrochemical hotspots with power plants. Levels of Zn, As, Se, Zr, Cs, Tl y Pb are relatively higher in the ceramic production areas studied. Source apportionment studies show high variability according to the type of sampling station. Between 4 and 6 PM sources were identified by means of the source contribution analysis, with the majority of the sources such as the crustal, industrial (with different chemical profiles according to the site), marine (only in the PM_{10} samples) and traffic factors being

common to all stations. At some sites there is a "combustion" factor, which accounts for the emissions from power plants, and/or an "external or regional" factor. The latter case includes emissions which are not generated locally with two different scenarios depending on the location: a) emissions from long distance transport, mainly characterised by the presence of ammonium sulphate and b) regional emissions, mostly defined by secondary inorganic aerosols, OM+EC and different trace metals.

INTRODUCTION

Due to the strong climatic and orographic contrasts found across the different regions in Spain, from the continental and mountainous interior to the Mediterranean and Atlantic coastlines and archipelagos (Canaries and Balearics), the composition and seasonal patterns of atmospheric particulate pollutants in urban areas of these regions can vary significantly. The factors controlling the variations of ambient air PM levels in Spain are of particular concern. PM_{10} levels in Spain contain a high proportion of resuspended anthropogenic and natural particles (Querol et al., 2004a).

The location of monitoring stations in the different EU state members is based on different strategies designed by each country, so that the number of stations in rural, urban, traffic or industrial sites varies greatly. According to Airbase data from 2001 to 2004 (http://air-climate.eionet.eu.int/), between 70-80% of the monitoring sites in Spain are located in hotspots, while in other EU state Members the average is 40-45%, although the average can be lower than 16% in some cases. As an obvious result of this, Spain, with a higher proportion of traffic and industrial hotspots monitoring sites, will present average annual PM_{10} levels and number of exceedences of the daily limit value higher than those countries with more rural and urban background monitoring sites. The difference is attributable to the fact that the monitoring of air quality in Spain was initially focused on the control of maximum exposure levels in urban environments, this explaining why the measuring sites were located in hotspots (i.e. places with a very high level of PM such as those close to heavy traffic and industrial emissions). The new directive, however, tries to evaluate the level of PM to which a representative population of 250,000 inhabitants is exposed. Nevertheless, it seems that the proposed $PM_{2.5}$ target/limit value is relatively permissive compared with the US $PM_{2.5}$ limit value, although it is very important to note that in EU the limit/target value also applies for hotspots.

With these current challenges and changes to European pollution law in mind (Putaud et al., 2004), this paper presents a summary of the results obtained from the PM pollution data collected over a period of 6 years (1999-2005) from a wide range of sites across Spain, greatly increasing the database used in previous investigations (Querol et al., 2004a) and better illustrating the factors controlling the flux of particulate matter across the country. A full report is publisher by the Spanish Ministry of the Environment (2006) in Spanish and English.

METHODOLOGY

The monitoring sites registered for the 1999-2005 time period were distributed across mainland Spain and the Canary and Balearic Islands, trying to cover all main types of different climatic conditions and anthropogenic activities. The areas located in the Iberian Peninsula include Galicia in the northwest, the Basque Country in the north, the eastern area bordering the Mediterranean sea, the central plateaux (both north and south interior Mesetas), Andalucía as the southernmost region of the Peninsula in the Atlantic-Mediterranean inter-phase and Extremadura in the central-western area next to Portugal. Both the Canary and Balearic islands were also selected, the former for their proximity to the Sahara desert, and the latter to illustrate PM levels at island

locations in the Western Mediterranean. The study includes 28 sites as described by Figure 1 and Table 1.

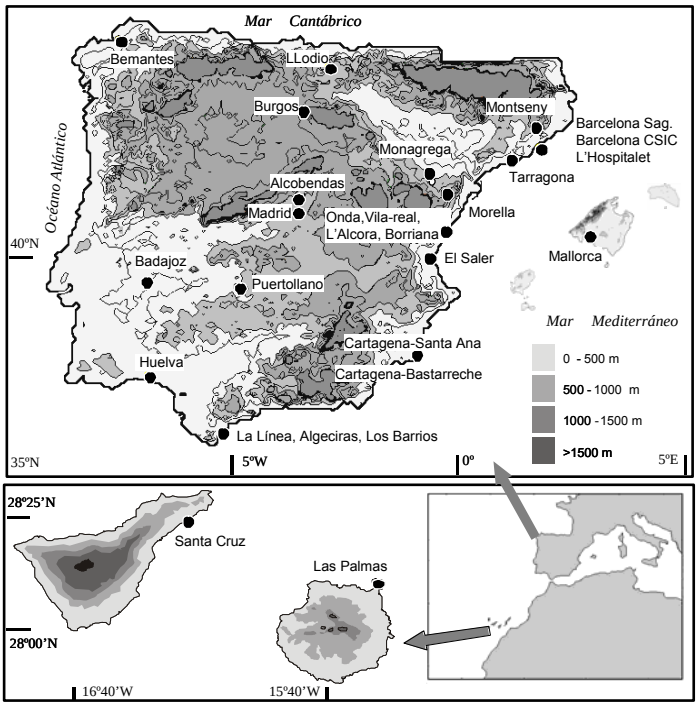

Figure 1. Location map of all monitoring stations across Spain discussed in this study.

The data were obtained using manual gravimetric PM_{10} high volume captors (in most cases the EU PM_{10} reference method EN12341 was used), and high or low volume samplers equipped with $PM_{2.5}$ inlets and quartz micro-fibre filters. The range of mean annual levels are summarised in Table 2. Following sampling, PM_{10} and $PM_{2.5}$ filters were analysed for major and trace elements and compounds, with a total of 57 determinations per sample (for specific conditions see Querol et al., 2004a). During this study the chemical components were grouped as: a) crustal (sum of Al_2O_3, SiO_2, CO_3^{2-}, Ca, Fe, K, Mg, Mn, Ti and P); b) marine (sum of Cl^-, Na^+ and marine sulphate); c) OM+EC or organic matter plus elemental carbon (value obtained after applying a 1.2 factor to the OC+EC concentrations for urban sites and 1.4 for regional background sites); and d) secondary inorganic species (SIC, as the sum of the non marine SO_4^{2-}, NO_3^- and NH_4^+ concentrations).

Receptor modelling techniques based on principal component analysis (PCA) and on a subsequent multilinear regression analysis (MLRA) were applied to the data bases for source apportionment analices at each sampling site following the methodology proponed by Thurston and Spengler (1985).

The influence of atmospheric transport scenarios on the levels of particulate matter was investigated by means of atmospheric back-trajectory analysis using the Hysplit model (Draxler and Rolph, 2003) and information obtained from TOMS-NASA, NRL, SKIRON and ICoD-DREAM aerosol and dust maps (TOMS, http://jwocky.gsfc.nasa.gov; NRL, http://www.nrlmry.navy.mil/aerosol; SKIRON: DREAM: http://forecast.uoa.gr; http://www.icod.org.mt/aerosol/dust, currently http://www.bsc.es/projects/earthscience/DREAM), and satellite images provided by the NASA SeaWIFS project (http://seawifs.gsfc.nasa.gov/SEAWIFS.html).

Table 1. Location and characteristics of the 28 measurement stations selected for the study.

Site	Longitude	Latitude	Altitude (m.a.s.l.)	Station Type	Sampling period
Alcobendas	03º 37' 39" W	40º 32' 42" N	667	Urban	2001
Algeciras	05º 27' 07" W	36º 08' 16" N	24	Urban-Industrial	2003-2004
Badajoz	06º 34' 48" W	38º 31' 48" N	188	Urban	2004
Barcelona-CSIC	02º 07' 09" E	41º 23' 05" N	68	Urban-Industrial	2002-2006
Barcelona-Sagrera	02º 11' 22" E	41º 25' 21" N	24	Traffic-Industrial	2001
Bemantes	08º 10' 50" W	43º 20' 15" N	170	Rural	2001
Borriana	00º 05' 10" W	39º 53' 38" N	20	Urban-industrial	2005
Burgos	03º 38' 15" W	42º 20' 06" N	889	Suburban	2004
Cartagena-Santa Ana	01º 00' 40" W	37º 39' 10" N	15	Suburban-Industrial	2004
Cartagena-Bastarreche	00º 58' 28" W	37º 36' 14" N	20	Urban-Industrial	2004
Huelva	05º 56' 24" W	37º 15' 21" N	10	Urban-Industrial	2001
L'Alcora	00º 12' 43" W	40º 04' 07" N	175	Urban-industrial	2002-2005
L'Hospitalet	02º 06' 40" W	41º 22' 23" N	70	Traffic-Industrial	1999-2000
La Línea	05º 20' 49" W	36º 09' 37" N	1	Urban-Industrial	2003-2004
Las Palmas	15º 24' 49" W	28º 08' 04" N	20	Urban	2001
Llodio	02º 57' 44" W	43º 08' 42" N	122	Urban-Industrial	2001
Los Barrios	05º 28' 55" W	36º 11' 02" N	45	Urban –Industrial	2003-2004
Madrid	03º 40' 52" W	40º 25' 32" N	672	Traffic	1999-2000
Mallorca	02º 35' 24" E	39º 35' 24" N	20	Suburban	2004
Monagrega	00º 19' 15" W	40º 56' 23" N	600	Rural	1999-2000
Montseny	02º 22' 40" E	41º 46' 47" N	730	Rural	2002-2006
Morella	00º 05' 34" W	40º 38' 10" N	1154	Rural	2004
Onda	00º 15' 09" W	39º 57' 44" N	163	Suburban-Industrial	2002-2005
Puertollano	04º 05' 19" W	38º 41' 64" N	670	Urban-Industrial	2004
Santa Cruz	16º 14' 51" W	28º 28' 21" N	52	Urban	2002-2006
Tarragona	01º 14' 52" E	41º 07' 29" N	20	Urban-Industrial	2001
Valencia- El Saler	00º 19' 08" W	30º 20' 46" N	7	Suburban coastal	2003-2004
Vila-real	00º 06' 21" W	39º 56' 30" N	60	Urban-Industrial	2002-2005

RESULTS AND INTERPRETATION

PM levels

According to the character of each monitoring site, PM_{10} and $PM_{2.5}$ concentrations (in $\mu g/m^3$ measured gravimetrically or corrected real time measurements) rise from: 13-21 and 8-14 (EMEP stations), 19-21 and 12-17 (rural), 28-32 and 18-25 (urban), 28-47 and 19-29 (urban-industrial background) to 46-50 and 28-35 (heavy traffic hotspots) (Figure 2 and Table 2). $PM_{2.5}$ concentrations are usually 40-75% those of PM_{10} at any given site. The $PM_{2.5}/PM_{10}$ ratios (Figure 2) measured at most sites of northern, north-western, north-eastern and central Spain fall in the range 0.6-0.7, with the highest ratios obtained in areas with higher pollution. This ratio decreases to 0.5 and 0.4 for most urban and rural sites of Southern Iberia and the Canary Islands, respectively, although again levels rise above this at heavily industrialised sites (0.6-0.7). The coarser grain size distribution trend shown in Figure 2 is probably the result of the higher mineral load in PM_{10} as a consequence of the drier climate and the proximity to the African desert regions.

At rural and regional background sites PM levels show concentration peaks coinciding with the intrusion of African air masses, regional atmospheric stagnation, and local contamination episodes, with a clear trend towards higher levels in summer due to resuspension, less precipitation and a higher frequency of African dust and regional

episodes (Millán et al., 1997; Viana et al., 2002; Escudero et al., 2005). The latter trend is illustrated by Figure 3 which shows the regular occurrence of a summer PM_{10} maximum over the last 11 years at our Monagrega site in east central Spain, as well as the common occurrence of a spring peak and a winter minimum (Rodríguez et al., 2001, 2004; Moreno et al., 2005). We calculate that 85% of all PM_{10} daily exceedences (>50 μg/m^3) at this monitoring regional background site over this period were caused by North African dust outbreaks. The oposite situation is observed in industrial and urban areas where, in most cases, around 70-80% of the exceedances are due exclusively to local anthropogenic sources. In these areas, the seasonal trend for PM levels is reverse to the one described above for the regional background, with higher winter levels as a consequence of the prevalence of atmospheric stagnation.

Table 2. Typical ranges of mean annual values (in μg/m^3 and in % in brackets) for PM_{10} and $PM_{2.5}$, and different components in Spain.

	PM_{10}	Crustal	OM+EC	SIC	SO_4^{2-}	NO_3^-	NH_4^+		Marine aerosol
EMEP stations	13-21	ND	ND	--	2-4	1-2	ND		
Rural background	19-21	2-5 (13-25%)	3-6 (13-29%)	5-8 (27-36%)	3-4 (15-18%)	1-3 (5-12%)	1.2-1.3 (6-7%)	Inland	0.7-1.7 (2-5%)
Urban background	28-32*	6-9* (21-28%)	5-10 (18-33%)	5-8 (18-27%)	2-4 (8-14%)	1.9-2.5 (6-8%)	1.1-1.6 (3-6%)	Coast & Balearic Islands	1.5-4.9 (3-12%)
Urban –industrial background	28-47	7-16+ (20-47%)	4-12 (12-26%)	6-13 (19-33%)	4-7 (12-19%)	1.1-5.5 (4-11%)	0.7-2.4 (2-6%)		
Traffic hotspots	46-50	13-15 (26-33%)	11-18 (25-37%)	8-15 (16-31%)	4-7 (9-14%)	2-6 (4-12%)	1.2-2.7 (3-5%)	Canary Islands	10-12 (25-27%)
	$PM_{2.5}$	Crustal	OM+EC	SIC	SO_4^{2-}	NO_3^-	NH_4^+		Marine aerosol
EMEP stations	8-14	ND	ND	--	ND	ND	ND		
Rural background	12-17	1.5-2.1 (11-12%)	4-5 (27%)	4-6 (31-36%)	2-3 (17-21%)	0.5-2 (3-11%)	1.2-1.4 (8-9%)	Inland	0.5-0.8 (1-4%)
Urban background	18-25	2-3 (11-17%)	5-9 (25-37%)	4-6 (21-36%)	2-4 (11-20%)	0.4-1.3 (2-6%)	0.7-1.9 (4-11%)	Coast & Balearic Islands	0.3-1.7 (2-5%)
Urban –industrial background	19-29	2-5 (9-22%)	4-11 (18-35%)	5-11 (22-33%)	4-5 (13-20%)	0.5-3.5 (3-10%)	0.9-2.5 (4-9%)		
Traffic hotspots	28-35	4-6 (12-16%)	12-17 (38-51%)	7-13 (19-37%)	4-6 (11-17%)	1-4 (4-11%)	1.4-3.2 (4-9%)	Canary Islands	1.4-1.6 (6-9%)

* Las Palmas de Gran Canaria excluded (44 μgPM_{10}/m^3) due to the high mineral load (12μg/m^3) caused by the frequent African dust outbreaks, as well as the high sea spray load (11 μg/m^3). Also excluded crustal contribution at Cartagena-Sta Ana, due to construction works around the monitoring site during the study period. + crustal load 7-12μg/m^3 (20-34%) if excluded ceramic area.

Figure 4 summarises the average annual PM_{10} concentrations registered for the 6 year recording period. Also shown on this diagram is the maximum annual limit value set by the European directive for 2005 (EU Directive 1999/30/EC). It can be seen that one third of the sites, with the 1999-2005 data, already exceed 2005 limit values, and only the rural background sites would meet the intended indicative limit values suggested by WHO (2005). Figure 4 also shows that the 25 μg$PM_{2.5}$/m^3 target value, proposed in the new directive and to be met from January 2010, is currently exceeded in a significant number of traffic and several industrial hotspots. If the mineral dust load, mainly of an anthropogenic origin but with higher levels in Spain compared with most central and northern EU state members (Querol et al., 2004b) due to the accumulation on roads by climatic causes such as low rainfall, is subtracted from the annual PM_{10} and $PM_{2.5}$ means, all the measurements performed in the 28 sites meet the requirements of the current and forthcoming EU directives, with the exception of 2 traffic and 1 industrial hotspots (Figure 4).

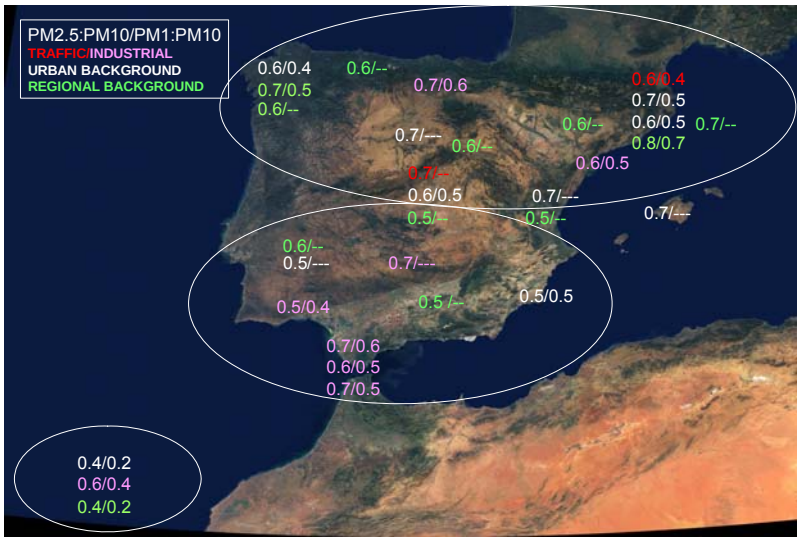

Figure 2. Average $PM_{2.5}/PM_{10}$ and PM_1/PM_{10} ratios indicating their regional, urban or traffic/industrial setting. Regional background data includes Spanish EMEP stations.

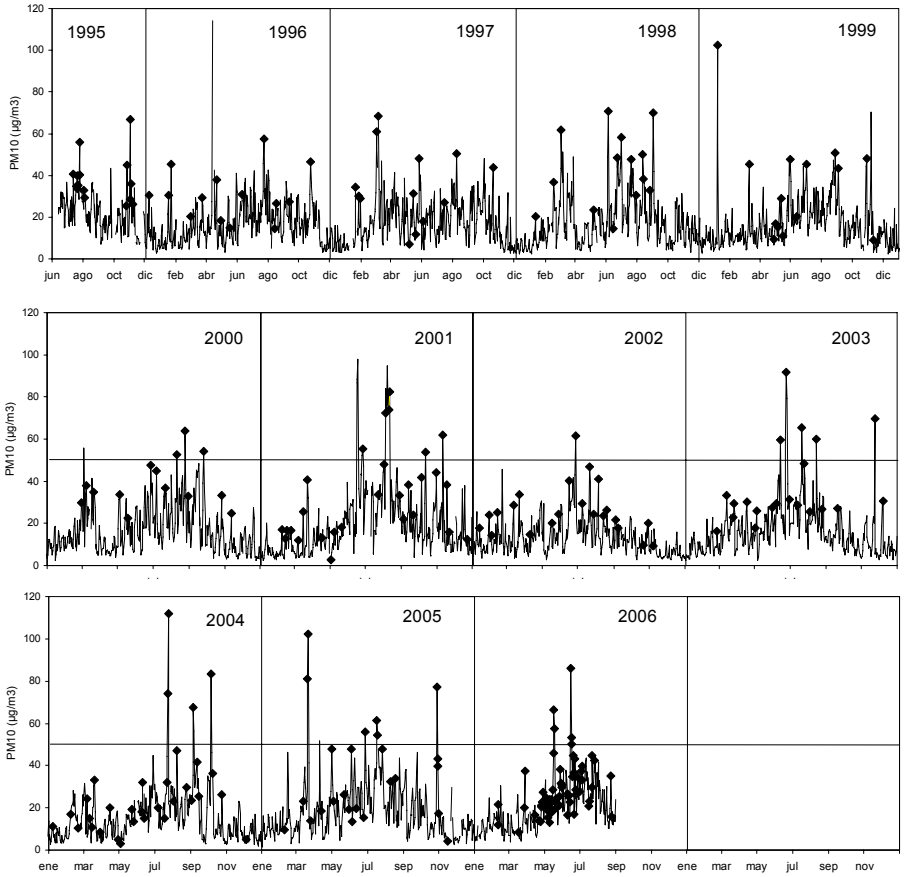

Figure 3. PM_{10} levels recorded from 1995 to 2006 at the Monagrega Regional background station and their relationship with the occurrence of African dust outbreaks (black rhombus), frequent during summer and in the February-March months. 54 out of 64 exceedances in these years were related to dust outbreaks. DLV: daily limit value.

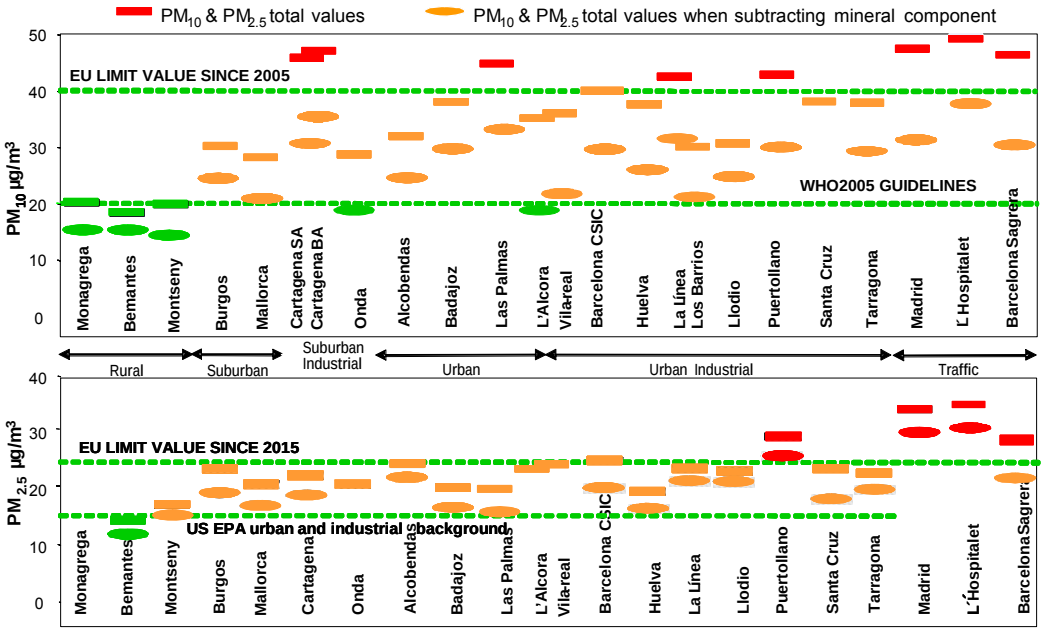

Figure 4. Top) Annual average PM_{10} values for each area studied across the country depending on the character of the site and compared with the allowed values for 2005 and the WHO 2005 air quality guidelines. Bottom) Same for the $PM_{2.5}$ values compared with the proposed limit value for 2015 and the US EPA limit value.

As we have discussed in previous publications (Querol et al., 2004c), and as is further illustrated by Figure 5, the current legislative daily PM_{10} limit value is more demanding than the annual limit value. Figure 5 plots all data on the annual PM_{10} and the values of the 90.4 percentile obtained in all PM monitoring sites of Spain in 2004 (a) and gives comparative data for elsewhere in Europe obtained from Airbase 2003 (b). The Figure unequivocally demonstrates how proposed limits on numbers of daily exceedences/year (currently 35 or 90.4 percentile) equivalent to the annual limit value of 40 $\mu gPM_{10}/m^3$ should be well over 60-65 $\mu gPM_{10}/m^3$, instead of the current 50 $\mu gPM_{10}/m^3$. Or in other words: a) to meet the requirement of 35 exceedances of the daily value of 50 $\mu gPM_{10}/m^3$, an annual mean of around 30 $\mu gPM_{10}/m^3$ should not be exceeded; or b) the number of annual exceedances of the 50 $\mu gPM_{10}/m^3$ daily limit value recorded by stations measuring 40 $\mu gPM_{10}/m^3$ as an annual mean is around 80, instead of 35. The 90.4 percentile and the annual mean are thus not independent variables and consequently only one of them should be standardised. If both of them are however to be standardised, then an annual mean of 40 $\mu g/m^3$ and a 90.4 percentile of around 60 $\mu g/m^3$ should be established. The fact that the same linear relationship is observed throughout Europe, with not very different slopes (1.356 for Spain in 2003, and 1.564 throughout Europe), indicates that the above discussion could be extrapolated across the rest of EU territory.

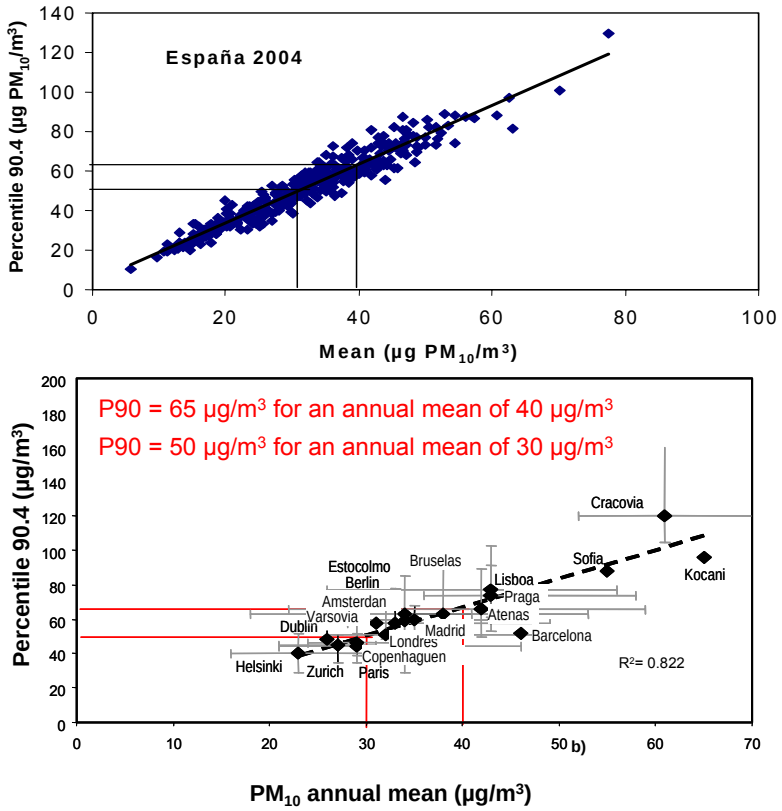

Figure 5. PM_{10} annual average levels against the percentile 90.4 values for a) all monitoring stations in Spain in 2004, and b) other main European stations (all data from Airbase, http://air-climate.eionet.eu.int/databases/airbase/index_html). See discussion in the text.

Major PM components

Carbonaceous particle concentrations (organic matter and elemental carbon) for both coarser and finer fractions rise from minimal background levels of 3-6 µg/m^3 (rural) to 5-10 µg/m^3 for most suburban and urban sites, except for the city traffic hotspots (up to 15 µg/m^3 in Madrid) and the petrochemical and coal mining town of Puertollano, where levels commonly exceed 10 µg/m^3. The highest levels are measured at traffic hotspots (Madrid and Barcelona: Figure 6 and Table 2). In addition to this obvious traffic and industrial influence, there are seasonal variations discernable at virtually all stations, with a carbonaceous particulate winter maximum (in both fractions) related to the low dispersive atmospheric conditions typical of that time of the year. This can be contrasted with a notable summer minimum, attributed to lower traffic flows and enhanced mixing conditions, which is also observed in the Canary Islands due in this case to the strengthening of trade winds enhancing dispersion of local pollutants. The OC/(OC+EC) ratios in urban sites of Spain are very high (0.6-0.8). If diesel vehicles are a major road traffic emission source and the OC/EC ratio of the PM emissions of these vehicles is usually low, a mismatch between the theoretical impact of these emissions on PM levels and the PM speciation is found.

In marked contrast to the finer size fractionation of carbonaceous particles, those elements normally associated with **mineral particles**, such as silicates, carbonates, oxides and phosphates ("crustal mineral particles"), are notably more abundant in the coarser fraction ($PM_{2.5-10}$). These PM_{10} components increase from <6 µg/m^3 in rural background stations, to 6-8 µg/m^3 at surburban sites, to >8 µg/m^3 at virtually all of the other sites (Figure 6 and Table 2), except for the ceramic industrial area (Onda, Vila-real, Borriana and L'Alcora), where 9 to 16 µg/m^3 of crustal load was measured as an

annual mean. The highest values (13-15 μg/m^3) are reached at the urban traffic hotspots and near primary industrial emission sources. The $PM_{2.5}$ mineral fraction is also clearly elevated near heavy traffic and specific industrial sites (4-6 μg/m^3 $PM_{2.5}$), although concentrations are always much lower than in the PM_{10} (13-15μg/m^3 PM_{10}). However, despite this decrease, it is important to emphasise the still high concentrations of fine ($PM_{2.5}$, and therefore more readily inhaled) crustal particles at traffic-rich and urban background sites, where levels range from 4 to 6 and 2 to 3 μg/m^3, respectively, as well as in some urban background monitoring stations in the Canaries (close to African dust emissions sources) which have recorded values of 3-5 μg/m^3.

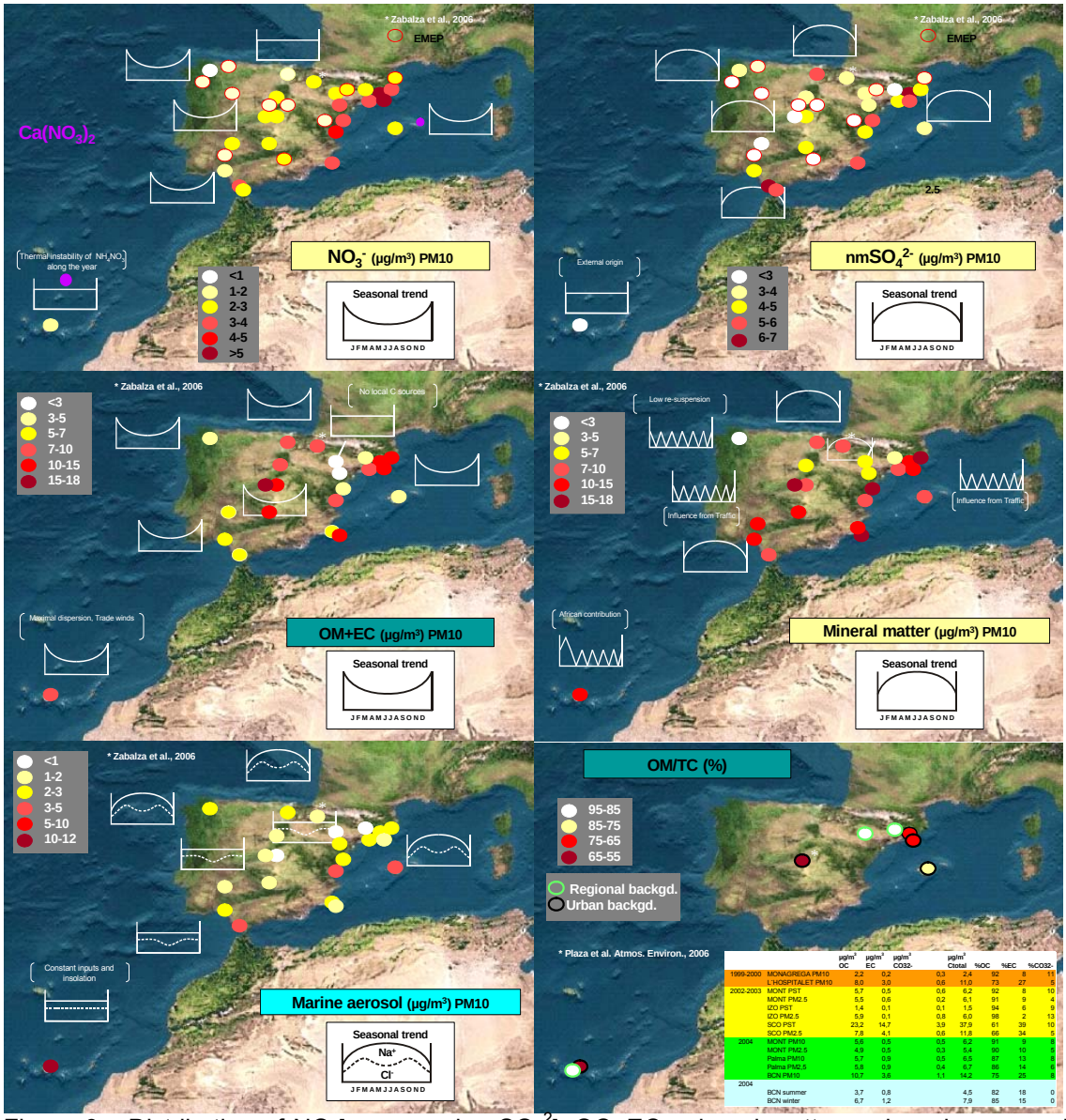

Figure 6a. Distribution of NO_3^-, non marine SO_4^{2-}, OC+EC, mineral matter and marine aerosol (sea spray) levels (μg/m^3) and OM/TC ratio (TC=OM+EC) across the country for PM_{10}. Seasonal trends are also shown when applicable.

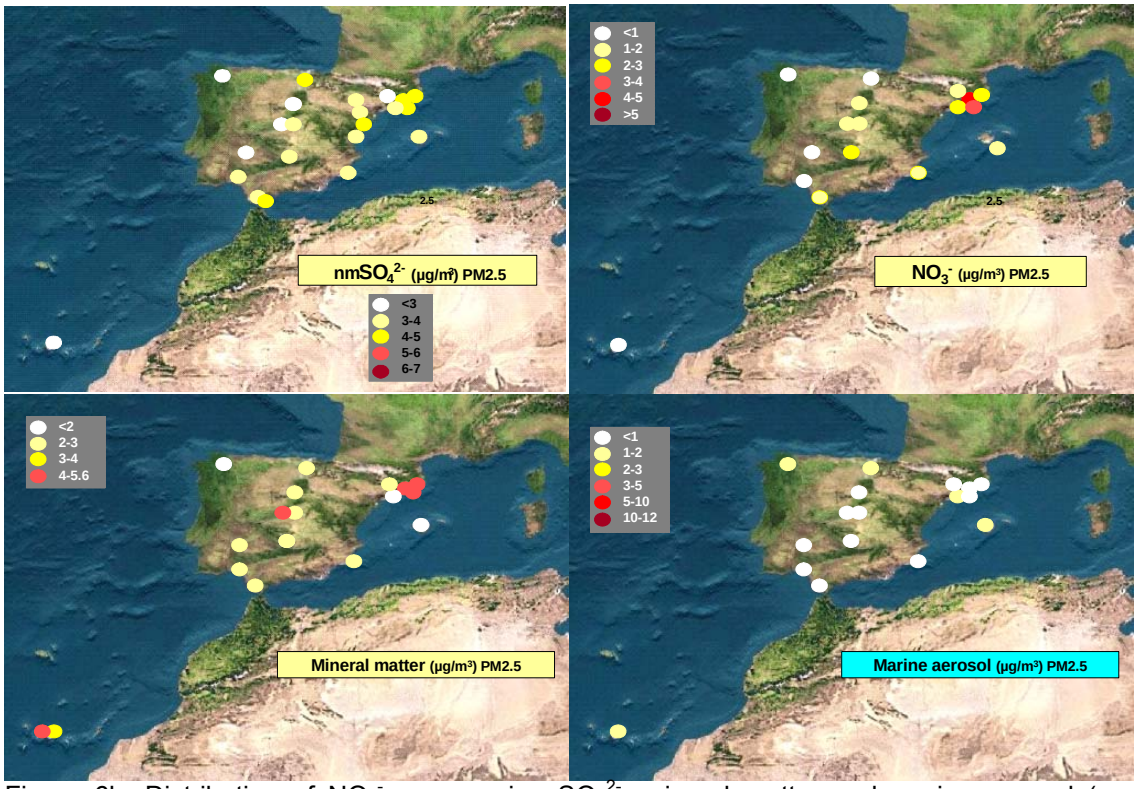

Figure 6b. Distribution of NO_3^-, non marine SO_4^{2-}, mineral matter and marine aerosol (sea spray) levels (µg/m^3) across the country for $PM_{2.5}$. Seasonal tendencies are also shown when applicable.

Figure 7 shows the annual mean concentrations of the major PM components versus PM_{10} and $PM_{2.5}$ levels. Notice how mineral dust is the PM component exhibiting the highest influence on the annual mean PM_{10} levels: it is the only component that always increases with increasing PM_{10} levels (from rural to suburban, urban-background, industrial and road traffic sites), and its contribution is as important as that (often higher than) of OC+EC and the sum of the SIC. The results indicate that as an average across the country, the increases in annual mean PM_{10} levels from rural to urban sites are mainly due to the increase in mineral dust load and OC+EC in PM_{10}. In the $PM_{2.5}$ fraction, all components exhibit an increasing trend with increasing general PM levels, but it is important to highlight that at the urban background sites and at the traffic hotspots the mean annual mineral levels in $PM_{2.5}$ reach 2-3 and 4-5 µg/m^3. This feature is not aplicable to most European regions as reported by Querol et al., (2004c) and recently confirmed by Rodríguez et al., (2007) using the same methodology (see Figure 8) in a Milan-London-Barcelona compartive $PM_{2.5}$ study. At London, mineral dust in $PM_{2.5}$ reached an annual mean of 0.8 µg/m^3, whereas at Barcelona, with a lower traffic flor this contribution reached 5 µg/m^3. At the urban areas, the high mineral dust load results from two main contributions: 1) mainly from high resuspension rates of road dust, and other dust sources such as demolition and construction, after its accumulation on roads because of the lower rainfall rates in Spain in comparison with central and northern EU regions, 2) in a much lower proportion from African dust events and natural resuspension on arid soils.

It has been demonstrated that the dust outbreaks have a high influence in the number of exceedances (Rodriguez et al., 2001; Querol et al., 2004a), but the present study indicates a lower influence on the annual means (<3 µgPM_{10}/m^3 of the annual mean), except for the Spanish regions close to Africa (southern and eastern Iberia, Canaries, Balearic) where the annual means are also highly influenced by natural contributions (3-5 µgPM_{10}/m^3 of the annual mean).

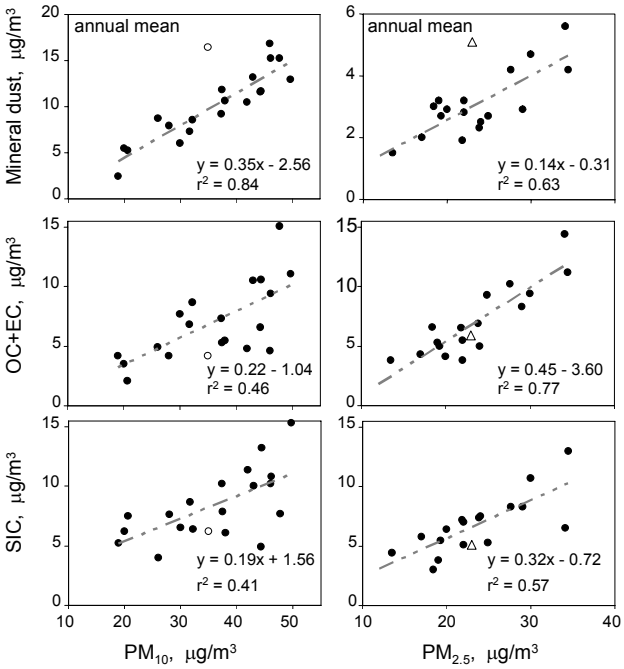

Figure 7. Annual mean levels of PM components versus PM_{10} and $PM_{2.5}$ levels across Spain (O: L'Alcora-industrial area of ceramic production and △: Santa Cruz de Tenerife urban-industrial background, none of them considered in the regression analysis).

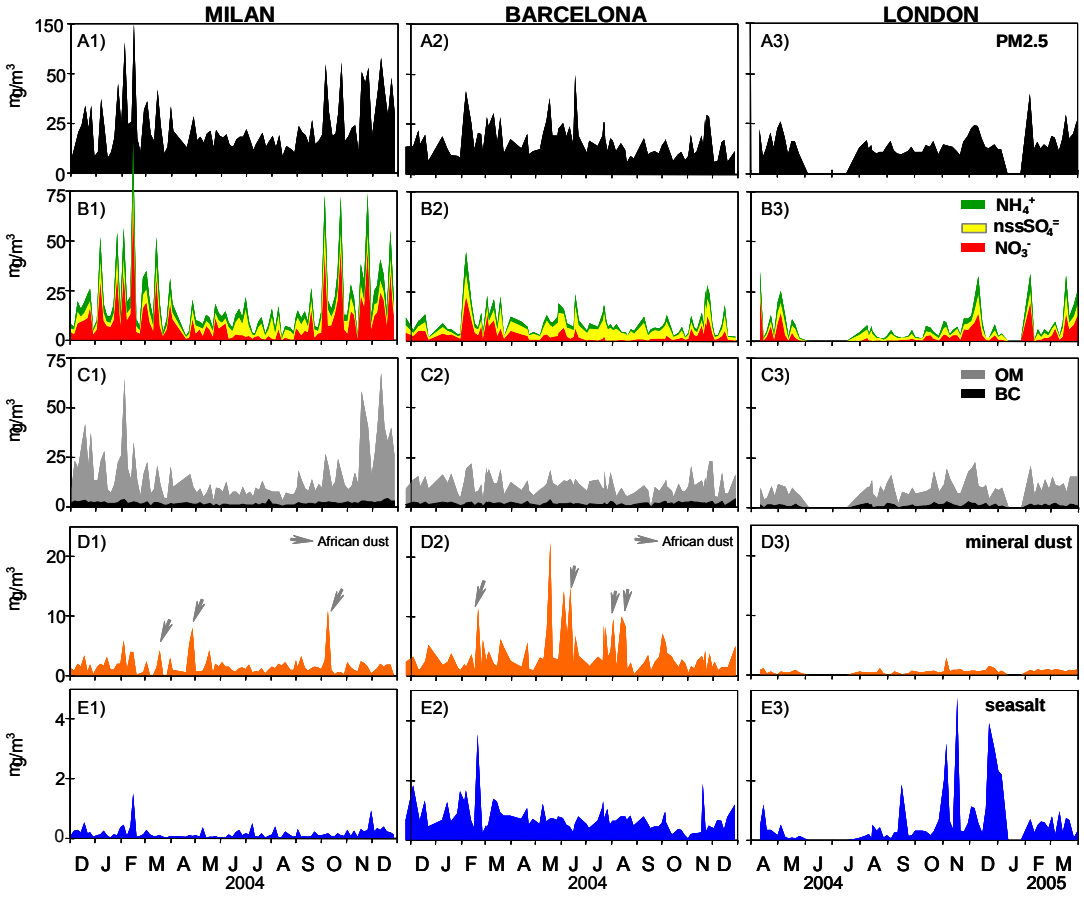

Figure 8. Comparison of PM2.5 speciation data from Milan, Barcelona and London obtained with the same methodology (Rodríguez et al., 2007), note the high mineral matter load at Barcelona, but the similarity of levels for the other PM components when compared with London.

The same preference for the coarser fraction is displayed by **sea spray**, which is predictably extremely low (around 1 µg/m^3 or less for PM_{10}) for inland sites, but more than double at the coast, reaching 11.5 µg/m^3 in the Canary Islands site at Las Palmas (Figure 6 and Table 2). The load of marine aerosols in PM_{10} in the Atlantic coastal sites is much higher than in the Mediterranean coast, with levels reaching up to 7 µg/m^3, as an annual mean contribution (Visser et al., 2001). PM_{10} measurements of Na^+ and Cl^- in the Canaries once again show the characteristic lack of seasonal variability, a clear difference from those recorded in the Peninsula where there are two distinct patterns. The first of these patterns is shown in the coastal sites (except Huelva) where Na^+ ions are at their maximum in summer due to the stronger influence of sea breezes, whereas Cl^- levels decrease during the summer months as a consequence of their volatilisation as HCl during the formation of $NaNO_3$ from gaseous HNO_3 and marine NaCl. The second pattern is observed in the sites located within the continental interior (Madrid and Monagrega) where the arrival of Na^+ and Cl^- as marine aerosol in areas far away from the coast occurs in a constant manner throughout the year, especially associated with the entrance of Atlantic fronts. In such places Cl^-/Na^+ ratios decrease during the summer months as a consequence of Cl^- volatilisation as HCl, as illustrated by Figure 9 which shows the typical Cl^-/Na^+ summer depletion in an inland site (Monagrega).

Levels of **secondary inorganic compounds** (sulphate, nitrate and ammonium salts) in PM_{10} measure <8 µg/m^3 at the majority of sampling stations, but exceed 10 µg/m^3 at several of the industrial and traffic hotspots, with the content in $PM_{2.5}$ being higher than the content in the coarse fraction (usually 65-85% of the content in PM_{10} is present in $PM_{2.5}$, Figure 6 and Table 2). Non-marine sulphate PM_{10} levels (mostly $(NH_4)_2SO_4$) are lower (<4 µg/m^3) in rural, suburban and urban background monitoring stations compared with traffic and industrial hotspots (4-7 µg/m^3), with the percentage of sulphate in $PM_{2.5}$ fraction always being higher than in the coarse (70% in $PM_{2.5}$). Within the Iberian Peninsula $(NH_4)_2SO_4$ levels are at their maximum in summer (Figure 9), because of the stronger insolation and therefore the higher oxidation of SO_2 to SO_4^{2-}. In the Canary Islands on the other hand, an elevated percentage of sulphate levels is not local in origin but due to emissions from urban and industrial sources in Europe having been rapidly transported over the ocean by the north-easterly trade winds (McGovern et al, 2002). Thus, sulphate aerosols in the Canaries are mostly externally derived and therefore lack seasonal variability.

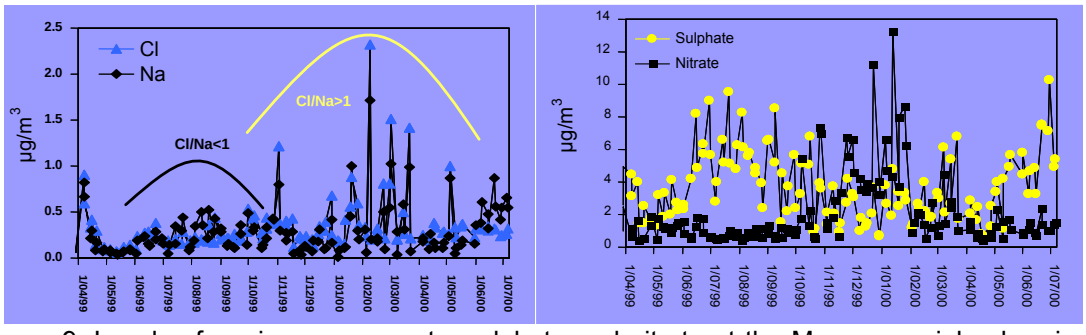

Figure 9. Levels of marine components, sulphate and nitrate at the Monagrega inland regional background station registered from April 1999 to July 2000.

Nitrate levels are characterised by a clear spatial gradient in concentrations across the Peninsula towards the Mediterranean region, (independently of the relevance of the regional/local emissions of NO_3^- precursors) (Figure 6). This trend is observed independently of the type of monitoring site studied, with sites under similar industrial emissions (like Huelva and Tarragona) showing very different average nitrate levels (2 versus 4 µg/m^3 in PM_{10} respectively). A possible cause of this spatial pattern is the higher ammonia levels along the Mediterranean coast, above all in the northeast of Spain, caused by emissions from intensive cultivation and farming (EPER, 2001).

However, traffic NH_3 emisssions in urban areas with high humidity (coastal areas in our case) may also give rise high ammonium nitrate levels. Within this context maximum levels (4-6 μg/m^3) are associated with the highly industrialised areas of the Mediterranean coast, while in the rest of industrial (the Atlantic sites of Huelva and Llodio), regional and urban background sites, nitrate levels vary between 2-3 μg/m^3, and the lowest values occur in the rural background site in North Spain (Bemantes, 1 μg/m^3). Seasonal variations show increased nitrate levels during winter, the opposite pattern to that shown by non-marine sulphates (Figure 8). This is probably due to the low thermal stability on NH_4NO_3 in summer, when under the prevalent warm conditions of most of the Iberian Peninsula, the formation of HNO_3 instead of NH_4NO_3 is favoured (Adams et al., 1999, Pakkanen et al., 1999; Schaap et al., 2002). This interpretation is supported by the lack of a seasonal pattern in northern Iberia and the Canary Islands due probably to mild summer and winter ambient conditions, respectively, compared with other regions of Spain.

A very peculiar feature is the large proportion of nitrate found in the coarse fraction of PM_{10} compared with other studies carried out in central and northern Europe (EC, 2004). The presence of gaseous HNO_3 and the possible interaction of this pollutant with mineral Ca carbonate and sea salt may account for the increase of the coarse nitrate proportion. The $PM_{2.5}$ nitrate fraction is always significantly lower than the coarser component (usually between 25-75%), this being due to the preference of $NaNO_3$ and $Ca(NO_3)_2$ for the coarser fraction (2.5-5.0 μm, Querol et al., 1998). In the Canary Islands, given the high ambient levels of NaCl, most of the nitrate is normally present as sodium (rather than ammonium) nitrate. Canarian nitrate levels are similar to those registered in the western Peninsula, and once again seasonal variation is less pronounced.

Levels of **ammonium** in both PM_{10} and $PM_{2.5}$ fractions register <2 μg/m^3 (Table 3) in all sites except those in Barcelona and Puertollano, and, unlike in most other elements described above, there is no preferential concentration in either fraction. As previously described, ammonium nitrate concentrations register minimum levels in summer in most of the sites, due to the thermal instability of ammonium nitrate and the corresponding presence of gaseous nitric acid and ammonia as the dominant phases. In winter, on the other hand, this compound is stable as a particulate aerosol, and its accumulation is favoured by less dispersive conditions in the atmosphere.

As an important conclusion of this study Table 3 shows the trace element concentration ranges measured for the elements studied in the 3 rural sites, 9 urban background sites and a number of industrial sites with different industrial influences. These concentration ranges may be of great value to evaluate the air quality in industrial areas concerning the concentration levels of some trace elements of environmental concern without limit or target values, or even to identify possible emissions of hazardous elements from a given industrial activity.

At the least polluted rural sites (Monagrega, Bemantes and Montseny), most trace metal concentrations lie within the range of 0.1-10 ng/m^3, with only Zr, Mo, Ni, V, Ti, Ba, Cu, Pb, Zn (in increasing order of abundance) exceeding 1 ng/m^3. Concentrations rise with increasing anthropogenic contamination, in the most extreme cases multiplying values to over x10 rural background for Ti, Cr, Mn, Cu, Zn, As, Sn, W and Pb.

Table 3. Concentration ranges for annual trace element levels (ng/m^3) in PM_{10} measured in rural and urban background sites of Spain, and in areas with different types of industry. Bold numbers are marked to highlight the trace markers from each type of environment.

ng/m^3	Rural background		Urban background		Steel	Stainless steel	Copper metallurgy	Zinc metallurgy	Petrochemical estates		Ceramic estates	
	min	max	min	max	mean	mean	mean	mean	min	max	min	max
Li	0.1	0.3	0.2	0.7	0.4	0.6	0.2	0,4	0.2	1.0	0.6	1.3
Be	0.01	0.02	0.02	0.05	0.06	0.03	0.07	0.06	0.01	0.07	0.02	0.05
Sc	0.1	0.1	0.1	0.3	0.1	0.2	0.1	0.10	0.1	0.3	0.3	0.5
Ti	7	22	18	**83**	24	36	60	31	23	62	33	57
V	2	5	2	15	8	**28**	7	11	7	**25**	4	5
Cr	1	2	2	8	**25**	**24**	2	2.9	2	6	3	8
Mn	5	5	4	23	**87**	17	11	12	8	11	6	8
Co	0.1	0.1	0.2	0.5	0.5	0.6	0.4	0.3	0.2	0.8	0.4	0.7
Ni	2	3	2	7	**33**	**20**	3	6.7	3	**11**	3	5
Cu	4	8	7	**81**	33	11	**70**	18	23	33	4	10
Zn	16	30	14	**106**	**417**	73	51	**504**	35	54	45	**183**
Ga	0.1	0.2	0.1	0.3	0.4	0.2	0.3	0.2	0.2	0.4	0.2	0.3
Ge	0.1	0.3	0.04	0.3	0.2	0.3	0.1	0.04	0.1	0.2	0.03	0.1
As	0.3	0.4	0.3	1.5	1.8	0.9	**5**	1.0	0.5	1.9	1.7	**5**
Se	0.3	0.5	0.3	1.1	**3**	0.8	1.5	0.6	0.5	0.6	1.0	**3**
Rb	0.5	0.6	0.5	1.8	1.1	0.8	1.5	0.9	0.6	1.6	1.2	2.4
Sr	1	5	3	**10**	3	6	4	7.8	4	5	3	5
Y	0.1	0.1	0.1	0.4	0.1	0.3	0.3	0.1	0.1	0.3	0.2	0.3
Zr	4	4	2	10	2	5	2	1.7	2	6	10	**20**
Nb	0.04	0.1	0.05	0.4	0.1	0.2	0.2	0.1	0.1	0.3	0.2	0.3
Mo	2	3	2	5	**15**	**15**	2	1.7	2	7	1	2
Cd	0.2	0.2	0.1	0.7	1.2	0.3	0.8	0.7	0.1	0.8	0.6	1.5
Sn	1	2	1	6	**38**	1	2	2.0	2	2	1	1
Sb	0.6	0.6	1	**11**	4	1	3	3.4	1	7	1	6
Cs	0.01	0.04	0.03	0.13	0.1	0.1	0.1	0.06	0.04	**0.2**	0.1	**0.3**
Ba	5	11	4	**41**	14	15	16	16	12	16	12	16
La	0.1	0.2	0.2	0.6	0.3	0.6	0.5	0.3	0.3	0.9	0.3	0.6
Ce	0.2	0.4	0.4	1.3	0.4	0.7	0.9	0.7	0.5	1.2	0.7	1.9
Pr	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.08	0.1	0.2	0.1	0.2
Hf	0.1	0.2	0.1	0.3	0.1	0.2	0.2	0.3	0.1	0.2	0.2	0.4
W	0.01	0.03	0.05	0.6	0.7	0.2	0.06	0.07	0.04	0.2	0.10	0.3
Tl	0.1	0.1	0.05	0.4	0.3	0.01	0.2	0.1	0.03	0.3	0.5	**2.8**
Pb	5	10	7	57	**102**	13	37	20	8	37	35	**103**
Bi	0.1	0.1	0.1	1.0	0.5	0.1	**1.6**	0.2	0.1	0.2	0.4	**1.5**
Th	0.1	0.2	0.1	0.3	0.1	0.1	0.4	0.1	0.1	0.4	0.1	0.2
U	0.1	0.2	0.1	0.3	0.3	0.1	0.3	0.2	0.1	0.3	0.1	0.1

The comparison of the usual concentration range for trace elements in urban areas and those measured at the above list of industrial regions allowed us to concluye the following evidences:

- Levels of Ba, Cu, Sb, Sr, Ti and Zn are relatively high in urban areas when compared with industrialised regions. This is probably due to the fact that in urban areas important PM emissions arise from brake (Cu, Fe, Zn, Sb), tyre (Ba and Zn) and road pavement (Sr and Ti) abrasion.

- Levels of Cr, Mn, Ni, Zn, Mo, Se, Sn and Pb are relatively high in steel production areas.
- Levels of V, Cr, Ni and Mo are relatively higher in areas where stainless steel is produced. Levels of V and Ni in this area (La Línea and Algeciras) may be also highly influenced by the petrochemical industry and fuel oil combustion (power generation and shipping emissions).
- Levels of As, Bi and Cu are relatively higher in areas with copper metallurgy industry.
- Leviels of Zn are relatively high at the zinc metallurgy hotspot (Cartagena). At this site leveles of V and Ni are also slightly high compared with other areas, but this is attributed to the emissions from a petrochemical estate or a fuel-oil power plant loscated in the same area.
- Levels of V and Ni are relatively high only in one of the areas with petrochemical plants (Algeciras-La Línea), but not in the others (Cartagena, Huelva, Puertollano and Tarragona) where the levels measured for these two elements fall in the usual range measured at urban sites. As previously stated the higher V and Ni levels measured at Algeciras and La Línea may be also attributed to fuel oil combustion: power generation and the intensive shipping emissions from the Gibraltar strait.
- The ceramic production area is characterised by a number of trace elements present in relatively high levels when compared with the usual range found in urban sites and also around other industrial activities. These elements are Zn, As, Se, Zr, Cs, Tl and Pb, and the reason for the higher concentrations is probably due to the frit, enamel and pigment production and applications.

Thus atmospheric metal particle mixtures from our sites tend to each have their own characteristic chemical signature. Furthermore, it is interesting to note that the ambient air levels of crustal related trace elements (Cs, Sr, Ti among others) measured as $PM_{2.5}$ reach only 20-40% the levels of PM_{10}, a percentage that in contrast increases up to 60, 65, 70 and 80% for As, Ni, Pb and Cd.

From the data available in thi study, we do not expect there will be major problems in the near future in meeting requirements from EU air quality directives concerning levels of metals in ambient air, out of a few specific industrial hotspots.

Source apportionment

Following the source apportionment analysis strategy described by Thurston and Spengler (1985), the different sources which contribute to the levels of PM_{10} and $PM_{2.5}$ were identified (Table 4), and their contributions have been quantified on a daily and annual basis for both samples at each station. Between 4 and 6 PM sources were identified by means of the source contribution analysis, the majority of the sources such as the crustal, industrial (with different chemical profiles according to the site), marine (only in the PM_{10} samples) and traffic factors were common to all stations. The crustal and traffic sources account for the same type of emissions at the different sites, whereas the industrial sources at sites such as Llodio, Huelva, Bastarreche, Palma de Mallorca and Puertollano depend on the different industrial activities. Furthermore, at four sites (A Coruña, Barcelona, Canaries and Puertollano) a "combustion" factor was defined, which accounts for the emissions from power plants. At the Llodio and Las Palmas (Canaries) stations, a factor defined as "external" was determined, which includes emissions which are not generated locally and are mainly characterised by the presence of ammonium sulfate (tracer of regional and long-range transport). Also a secondary-regional factor, not easily linked to any specific emission source, was defined at Burgos, Badajoz, Santa Ana, Bastarreche and Puertollano mostly defined by secondary inorganic aerosols, different trace metals and OM+EC, depending on each site.

As expected, the contribution of the different sources is highly variable according to the type of sampling station. The results obtained at the sites in the Iberian Peninsula are also very different from those obtained in the Canary Islands. The results of the source apportionment analysis of particulate matter are presented as an example of the outputs of the studies performed. Main points may be summarised as follows:

- Direct road traffic contributions reach from 30-48% of the PM_{10} annual load in urban sites, not including secondary aerosols which are formed from gaseous precursors from traffic. These values can be lower (e.g. 21%) in some urban sites such as Badajoz where crustal and secondary particles are predominant.
- Industrial contributions reach, in most industrial areas, loads close to 30% of the PM_{10} annual values. Exceptional high values can be registered at sites with high industrial influence (44% in Puertollano).
- There is an important and constantly identified source of crustal composition which is in fact not a single source but includes a mixture of natural and anthropogenic mineral matter (road dust, demolition and construction dust among others) deposited in urban areas and constantly being resuspended by traffic and wind. This load represents 25 to 35% of the PM_{10} mass in urban areas, but can reach up to 50% around industrial areas with primary particulate emissions (ceramics). It is important to note the marked North to South increasing gradient found when looking at mineral matter levels in PM_{10} as aridity (caused by low rainfall rates) and proximity to Africa increases.
- The marine contribution is limited to 3-5% in continental sites, 4-10% in coastal sites, but reaches 30-35% in urban sites of the Canary Islands on an mean annual basis. These high percentages are due to a relatively low PM_{10} concentrations and high Atlantic wind speeds.
- There is a large contribution of unaccounted mass for model outputs obtained for regional background sites. This is attributed to the relatively high proportion of water contained in PM_{10} which is still not extracted from the sample under 25 or 50% humidity chambers after 48 h of equilibrium. This artefact is inherent to the filter sampling strategy and is more important in remote sites due to the lower ambient concentrations of actual PM components compared with absorbed water with respect to the polluted sites.
- Another limitation we found from our source apportionment studies is the frequent identification of a secondary inorganic aerosol (SIA) regional contribution source resulting in lower loadings of other components. This may account for up to 30% of the PM_{10} levels and is in fact a regional or external source stemming from a mixture of contributions, not a single source. The relative load of this mixed sources component is lower in polluted sites because part of its contribution is assigned by modelling to local emission sources that are partially associated with SIA and with defined chemical tracers.
- There is an increasing gradient from the lower levels of the Atlantic side to relatively higher levels in the Mediterranean coast of Spain concerning the SIA load on a regional scale. This is attributed to lower dispersion of pollutants, lower rainfall, and probably to higher NH_3 levels (due to agricultural emissions) in the eastern part of the country. Thus the origin of this higher secondary inorganic load is due to relatively high NO_x and SO_2 emissions from industry and urban sources, to the higher NH_3 agricultural emissions, and probably to the higher humidity in eastern Spain.

Natural sources have a much higher influence on PM_{10} levels in the Canary Islands than in the Peninsula. The marine source represents 35% of the PM_{10} mass in the Canaries (12 $\mu g/m^3$), but only 3–15% in the Peninsula (0.7–3.4 $\mu g/m^3$). In the Central regions (Madrid and Monagrega), this fraction contributes with only 0.5–1.0 $\mu g/m^3$ whereas in the coastal areas it reaches 2–3 $\mu g/m^3$. Finally, the crustal load in PM_{10}

ranges from 16–36% at all sites, including the one in the Canary Islands (33%). However, in absolute values, the contribution of the crustal factor is maximal in the Canary Islands 11–15 μg/m^3. In this case, a high proportion of the crustal contribution has an African origin (mean daily dust loads reaching 100–600 μg PM_{10}/m^3 are often recorded during the frequent African episodes, known locally as "calima"). The crustal component at the Barcelona and Puertollano stations attained similar values (15 μg/m^3). However, this is due to road dust resuspension and other mineral emissions rather than to African contributions. Moreover, crustal contributions at urban stations (Escuelas Aguirre-Madrid, Huelva, Tarragona, Llodio, L'Hospitalet, Badajoz) are high (8–12 μg/m^3).

Table 4. Results of the source apportionment analysis (% contribution to mean annual PM mass levels) performed for PM_{10} (top) and $PM_{2.5}$ (bottom) in different monitoring sites of Spain.

PM_{10}	Montseny	Monagrega	Bemantes	Palma	Huelva	Alcobendas	Llodio	Las Palmas	Tarragona
Crustal	23	26	12	16	27	31	26	33	32
Regional	58	26	24	20	<1	22	19	10	<1
Traffic	<1	13	25	31	33	34	22	5	30
Marine	9	5	14	16	5	6	7	35	9
Industrial	<1	<1	17	15	32	6	15	10	28
Not det.	8	30	8	2	3	1	11	7	1

PM_{10}	Madrid	L'Hospitalet	Barcelona	Cart. Bast.	Burgos	Badajoz	Puertollano	Los Barrios	Algeciras
Crustal	26	24	32	25	24	32	36	27	25
Regional	18	<1	<1	17	26	20	<1	<1	<1
Traffic	48	35	32	19	10	21	<1	26	18
Marine	3	4	5	3	3	4	9	15	17
Industrial	<1	24	30	5	23	9	44	31	37
Not det.	5	13	1	31	14	14	11	1	3

$PM_{2.5}$	Badajoz	Palma	L'Hospitalet	Burgos	Carta. S.A.	Puertollano	Badajoz
Crustal	22	19	9	14	9	6	22
Regional	30	30	<1	30	<1	<1	30
Traffic	28	21	53	9	40	<1	28
Marine	<1	<1	<1	<1	2	<1	<1
Industrial	3	8	35	20	27	59	3
Not det.	17	22	3	27	22	35	17

The crustal load for days with African dust outbreaks at remote sites is much higher (12-15 and 2.5-5 μg/m^3 for PM_{10} and $PM_{2.5}$, respectively as annual means) than the annual mean 3-5.5 and 1.3-3 μg/m^3 for PM_{10} and $PM_{2.5}$) and especially than for non African days (1-4 and 1-2 μg/m^3 for PM_{10} and $PM_{2.5}$). With these data one may calculate that the regional soil resuspension may account for around 1-4 and 1-2 μg/m^3 as annual PM_{10} and $PM_{2.5}$ means, whereas the African dust contribution to the mean annual levels may reach 1-2 and 0.3-1 μg/m^3 for PM_{10} and $PM_{2.5}$, in central and northern Iberia. Higher African dust contributions are expected for the Balearic and Canary Islands and Southern Iberia.

If we subtract the 5.5 μg/m^3 crustal contribution detected at the Monagrega rural station (regional dust resuspensión: local and African) from the urban background levels of crustal material, it may be concluded that there is a local urban crustal contribution of 2–7 μg/m^3 at urban sites. This contribution is therefore related to the mineral city background arising from anthropogenic activities (demolition, construction, road works, traffic). If we subtract the levels of crustal components recorded at urban background from those attained at roadside sites it can be concluded that the local pavement erosion of the monitored road accounts for 3–5 μg/m^3 of crustal input to the annual PM_{10} mean levels. Thus, an important proportion of the crustal load quantified with the receptor modelling may be attributed to urban anthropogenic sources such as traffic. Road dust may be deposited onto the pavement and, in the absence of rain episodes, the resuspension of this dust could increase the crustal load of PM_{10}. The source receptor model will not always associate this dust with traffic tracers such as nitrate or carbonaceous aerosols.

The same emission sources found to be responsible for major variations of PM_{10} levels were identified for $PM_{2.5}$ using the factor analysis. However, as discussed above, the marine and the crustal factor contributions were markedly reduced with respect to PM_{10}. However, in relative values, the crustal contribution may still account for around 20% of the $PM_{2.5}$ mass, especially at kerbside sites.

Additional remarks: PM_{10}, $PM_{2.5}$ and PM_1

The coarse fraction ($PM_{10-2.5}$) is dominantly made up of mineral dust (with variable origin) and marine aerosol, although variable relative minor proportions of SIA (Na, Ca, K, Mg sulphate and nitrate) and carbonaceous material may be also present. It is evidenced from several studies that at drier and warmer regions of Europe the coarse/fine fraction of SIA increases with respect to the cooler and wet regions.

The mass of marine aerosol and mineral dust is reduced in the $PM_{2.5}$ fraction with respect to PM_{10}, specially the first one. However, in drier and warm regions of Europe the contribution of mineral dust to $PM_{2.5}$ may still reach 15-20%. Most of the carbonaceous components presents in PM_{10} fall also in the $PM_{2.5}$ range, but as previously stated a fraction of the sulphate, and specially sulphate, loads of PM_{10} is coarse, and consequently is not present in $PM_{2.5}$. Thus, $PM_{2.5}$ is still a mixture of SIA, carbonaceous material and variable proportions of mineral dust depending on the region of Europe. In industrial hotspots with important primary PM emissions, the mineral load in $PM_{2.5}$ may still be very high (up to 40% of the bulk PM2.5 mass around cement, ceramic production areas or mining activity).

The mineral dust load is markedly reduced if PM_1, thus even in Southern Europe, the mineral matter load in PM1 measured at urban sites is lower than 1 $\mu gPM_1/m^3$, much reduced than in $PM_{2.5}$ (2-6 $\mu gPM_{2.5}/m^3$). Around 80-90% of the carbonaceous material present in $PM_{2.5}$ is still present in PM_1. However, SIA (especially nitrate levels) are reduced from $PM_{2.5}$ to PM_1 by a 20-30%. Thus, the $PM_{2.5-1}$ fraction is made up mineral dust and SIA, with a minor fraction of carbonaceous mineral matter.

As a summary, it can be stated that in most urban areas of Europe (see Figure 10, showing data from Barcelona, Spain, as an example):

a) PM_1/PM_{10} and $PM_{2.5}/PM_{10}$ proportions vary widely across Europe, but in most urban areas these falls in the ranges: 40-60 % and 60-75%, respectively.
b) Carbonaceous material it is mainly present in the fine fraction (80/20/<1% in the $PM_1/PM_{2\text{-}5\text{-}1}/PM_{2.5\text{-}10}$, fractions respectively).
c) Conversely, mineral dust and sea spray aerosols are mainly coarse in size (10/20-25/65-70% in the $PM_1/PM_{2\text{-}5\text{-}1}/PM_{2.5\text{-}10}$, fractions respectively, in both cases).
d) Sulphate is distributed among the three PM fractions with a prevalent fine grain size (65-70/20-25/10% in the $PM_1/PM_{2\text{-}5\text{-}1}/PM_{2.5\text{-}10}$, fractions respectively), as a consequence of the prevalence of ammonium sulphate (fine aerosols) versus the coarser Ca, Na or Mg sulphate species.
e) Nitrate shows a similar size distribution to sulphate, with a shift towards the coarse fractions (45-60/20-25/20-35% in the $PM_1/PM_{2\text{-}5\text{-}1}/PM_{2.5\text{-}10}$, fractions respectively). 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.
f) Ammonium shows a fine size distribution (75-80/20-25/<5% in the $PM_1/PM_{2\text{-}5\text{-}1}/PM_{2.5\text{-}10}$, fractions respectively) as a consequence of the fine grain size of ammonium sulphate and nitrate.

g) The unaccounted mass follows a very similar size distribution to that reported for nitrate and sulphate (50-70/10-15/20-40% in the $PM_1/PM_{2-5-1}/PM_{2.5-10}$, fractions respectively). These species are very hydrophilic and tend to accumulate water (the main cause of the unaccounted determination).

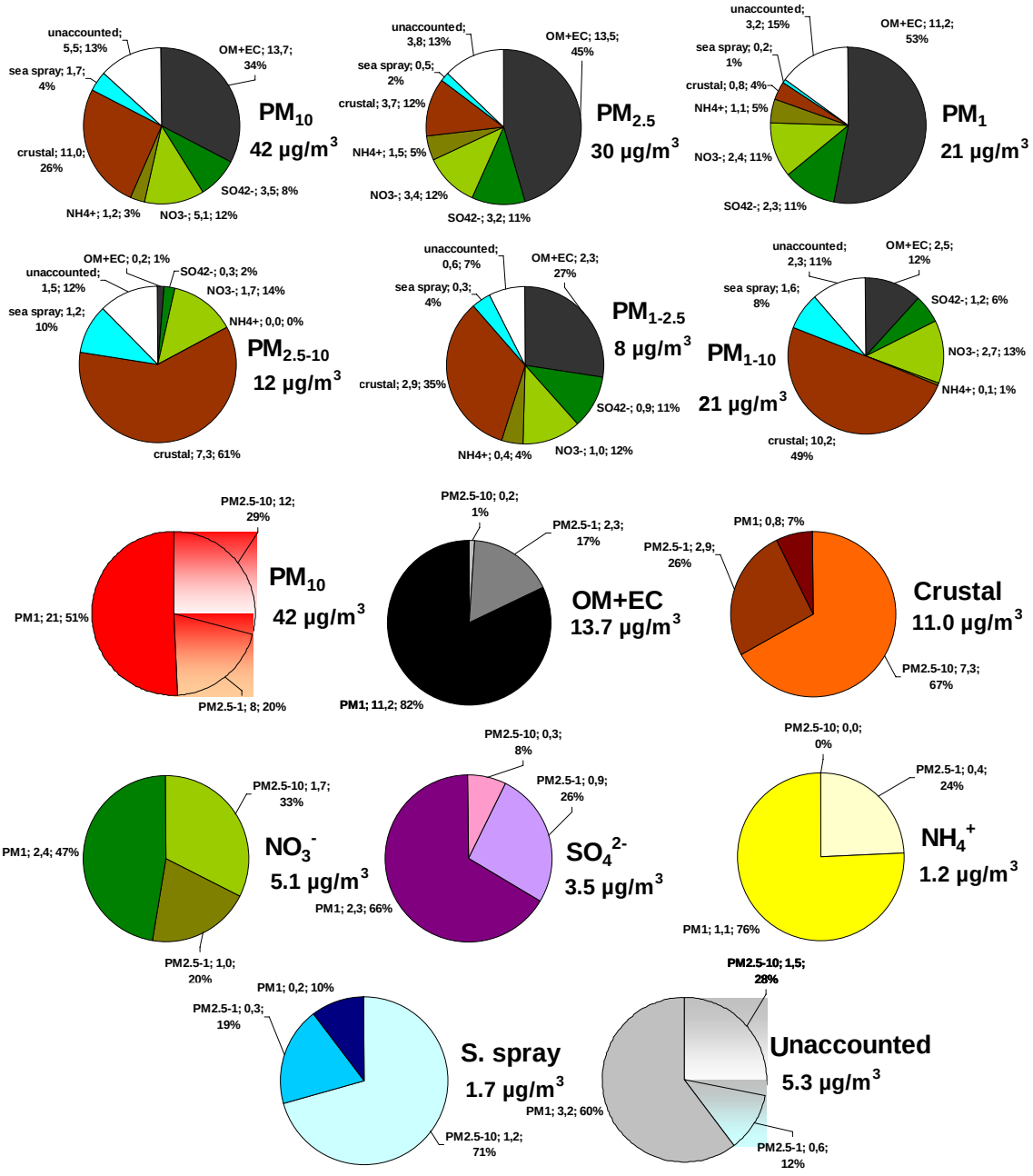

Figure 10. Mean speciation data for PM_{10}, $PM_{2.5}$ and PM_1 obtained at an urban background site of Barcelona, from 10-10-2005 to 08-01-2006, n=22 samples for each of the 3 PM fractions obtained simultaneously. $PM_{2.5-10}$ and $PM_{1-2.5}$ obtained by difference.

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