

Natural and Anthropogenic Contributions to PM₁₀ and PM_{2.5} in an Urban Area in the Western Mediterranean Coast

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Received: 4 September 2007 / Accepted: 16 February 2008 / Published online: 14 March 2008
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Abstract Source apportionment analysis was used to identify the factors contributing to atmospheric pollution at a monitoring location in the Southeast of Spain, a well documented area with an arid climate and high insolation favouring two sources of particulate matter: secondary transformation in the atmosphere and resuspension of crustal dry soils to the air. These conditions are further complicated by numerous industrial facilities in the area of the historical city of Cartagena. This paper describes the air quality of an area which includes a zinc metallurgical industry, a petrochemical factory, an oil power station, a shipyard and natural phenomena including African dust transport and resuspension of regional and/or local crustal materials. Major and trace element concentrations in PM₁₀ and PM_{2.5} were determined at two monitoring stations in Cartagena (one PM₁₀ sampler located at a traffic hotspot and the PM_{2.5} sampler at a suburban station), during 2004 and 2005. Results showed that in the PM₁₀ fraction, the zinc metallurgical activity

was linked to high levels of Cd, Zn and Pb; shipyard emission was associated with high levels of Cr and Ni; and high Ni and V levels were associated with the secondary aerosol indicating the contribution from oil combustion (oil-fired power station or petrochemical facilities). In the PM_{2.5} size fraction, the zinc source is defined by Zn and Pb; V, Ni and As appear with the oil combustion emissions. In contrast to PM₁₀, shipyard activity is not consistently defined. Consistent sources found in both size fractions include crustal materials and traffic emissions.

Keywords Receptor modelling · Shipyard emissions · Tracer elements · Zinc metallurgical emissions

1 Introduction

Suspended particulate matter (PM) is one of the pollutants which require monitoring as a component of the strategy to manage the risk motivated by its health, ecological and civil impacts (Molnár and Mészáros 2001; Reis et al. 2002; Bates et al. 2005; Künzli et al. 2005; EPA 2006). Major sources of aerosols are heterogeneous in size and composition (Pacyna 1986), making it possible to attribute each fraction of the mass collected on a filter to a suspected source using knowledge of its chemical composition. Furthermore, if there are several contributors of specific chemical species, the relative load of each chemical species within the source emission may still

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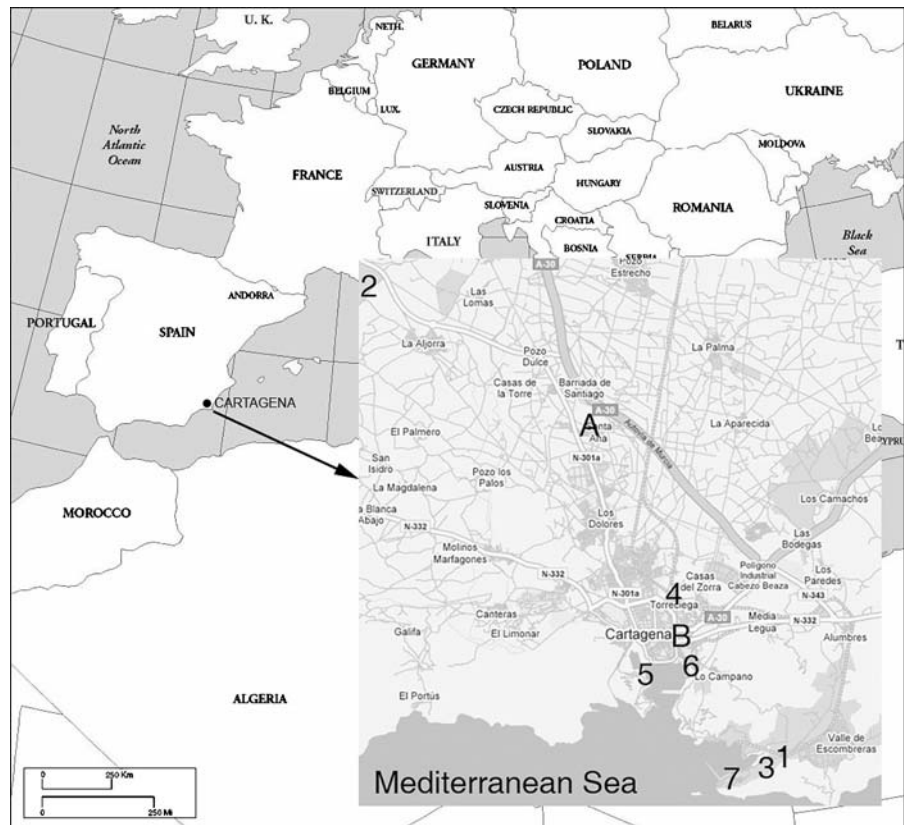
allow the scientist to identify the individual sources in a single aerosol sample (Li et al. 2003). Receptor modelling techniques are useful tools for identifying individual sources in a sample of atmospheric pollution.

The analysis of the sources contributing to PM levels in Cartagena is especially interesting given the complex mixture of anthropogenic and natural emissions in the area. Figure 1 shows the locations of the major sources in the Cartagena area including (1) harbour activities, (2) a petrochemical factory, (3) a plastic production factory, (4) a power station (sometimes assisted by oil combustion), (5) a Zn metallurgical industry, (6) a military shipyard, (7) dust outbreaks from the northern African deserts, and (8) resuspension of local and/or regional particulate matter from a variety of origins. The major sources of resuspended PM include: (1) soils with variable Pb, Zn, Cd or Cu content in the vicinity of the city (Martínez García et al. 2001) under the influence of the persistent aridity, this is due to a climate with mild temperature and scarce precipitation during the year

and extremely low precipitation in summer, when temperature and insolation are maximal (Capel Molina 1986); (2) agriculture in the surrounding area named “El Campo de Cartagena”; and (3) resuspension of city dust (mainly from construction and demolition activities).

In 1979 Cartagena was declared “area of atmospheric pollution”, this term supposed a series of legal and subsequent technical measures in order to reduce the concentration of sulphur dioxide and suspended particulate matter; these pollutants were overcoming their thresholds in a way enough to motivate the mentioned response from the Spanish Government (Decreto 833/1975, 6 February. BOE-Official Spanish Gazette- 96, 4/22/1975 and Real Decreto 1197/1979, 20 February. BOE-Official Spanish Gazette-123, 5/ 23/1979). Although the situation had improved by the early 80s, the air quality was still undesirable (Moreno-Grau 2006). Harbour activities including the unloading of soybean gave rise to several epidemic pollution episodes, with the result of one fatality during an episode in 1987 (Consejería de

Fig. 1 Plot of the main locations in the survey. 1 Petrochemical factory, 2 plastic production factory, 3 power station, 4 zinc metallurgical industry, 5 military shipyard, 6 city dock, 7 Escombreras dock; A PM_{2.5} Santa Ana sampling station, B PM₁₀ Bastarreche sampling station



Sanidad de la Región de Murcia 1991). As a consequence of these episodes, the regional authorities implemented a strategic plan which reduces or stops factory emissions during meteorological conditions associated with elevated pollutant levels in the Cartagena atmosphere (Cirera 2005).

The implementation of air quality measures should pay attention to source contribution analysis, as it points to the contributing sources which should be addressed (Querol et al. 2001a). Source contributing studies can establish a robust knowledge base needed for the design of the policies or strategies that minimize the impact of anthropogenic emissions and identify the episodes with a natural origin. As part of the effort to implement the assessment and control of the atmospheric pollution in Cartagena, this paper characterizes the complexity of the aerosol and applies statistical models for identifying the multiple sources.

2 Materials and Methods

2.1 Experimental

Two aerosol monitoring locations belonging to the Cartagena Local Council were chosen for this survey: Bastarreche and Santa Ana (Fig. 1). PM₁₀ sampling (DIGITEL DHA-80, Switzerland) was performed at the hotspot traffic monitoring station at “Bastarreche Square”, an entrance from a highway to the city, near the coach and train stations (20 m a.s.l). This sampling lasted from February 25, 2004 to March 15, 2005 with a total of 98 samples were collected on quartz micro-fibre filters (Schleicher & Schuell QF20, Germany). PM_{2.5} sampling was carried out at the suburban monitoring station at “Santa Ana”, a small village around 3 km from Cartagena. Sampling at this site lasted from January 16, 2004 to March 2, 2005 with a total of 98 samples collected with the same filters and sampler.

Once sampled, the filters were sent to laboratory to determine PM ambient air concentrations, according to the procedure described in Querol et al. (2004a,b): The methodology included the successful performance of an IEA round robin exercise, the use of reference material in keeping with relative analytical errors lower than 10% for most elements. The analytical methods include (a) PM levels were determined by gravimetry; (b) Major and trace chemical species determined by acid digestion and

further analysis by ICP-MS, and ICP-AES; (c) Soluble anions were determined by water leaching and analysis by ion chromatography, and ammonium by FIA colorimetry; and (d) Organic matter and elemental carbon (OM+EC) were determined by applying a factor of 1.2 to the total C content determined in a CHNS elemental analyser (Turpin et al. 2000).

2.2 Statistical Treatment and Source Contribution Method

One approach to receptor modelling is based on factor analysis (FA). The FA applied in this study is principal component analysis (PCA; Thurston and Spengler 1985). The results obtained with this analysis were then interpreted using complementary information from meteorological data and back-trajectory analysis (Draxler and Hess 2004), satellite imagery (McClain et al. 1998), as well as support from regional dust modelling (Kallos et al. 1997; Nickovic et al. 2001; NRL 2003). The purpose of FA is to reduce the number of dimensions in data sets containing a large number of variables in order to facilitate the interpretation of the observed aerosol (Hopke 1992). To aid in the interpretation of the main common factors, the PCA method was applied with a varimax rotation to the set of data of the chemical species. The result was the production of a number of independent factors that maximize and minimize the associations between individual variables and factors. Each factor can be described as a linear combination of the studied variables (i.e. their loadings; Hopke 1992). The decision of selecting the number of factors in the analysis was based on the eigenvalue for the factors. For this study, factors having an eigenvalue greater than 1 were retained in the model.

After the identification of the probable source of a factor (based on the elements with high factor loadings; Tanner and Wong 2000), its quantitative contribution to total measured PM was described according to a multilinear regression analysis (MLRA; Harrison et al. 1996). The final products of the analysis were equations that predict the contribution of each source for each variable in every sampled day.

2.3 Atmospheric Transport Scenarios

Five day air mass isentropic back-trajectories supported by the HYSPLIT-4 Model (Draxler and Hess

2004) were run at 750, 1,500 and 2,500 m a.s.l. in Cartagena. This tool identified the geographical characterization of air masses as one of the eight sectors appearing in Fig. 2. Most of the time (36% of days in 2004), Cartagena is under Atlantic conditions (including North Atlantic, Northwest Atlantic and West Atlantic air masses) which do not produce remarkably high level episodes for PM₁₀ or PM_{2.5} sizes. On the other hand, Southwest Atlantic air masses (4% of days in 2004) usually present marked increased levels, probably because of the contribution of African dust. PM levels are the highest with air masses arriving directly from Africa (29% of days in 2004) implying high levels of crustal aerosols. When micro and mesoscale conditions predominate (15% of days in 2004), apart from the intensification of secondary processes (Querol et al. 2004a), there is a stagnation which leads to resuspension of regional material (Gangoiti et al. 2001). It is also possible that sulphate enriched masses reach Spain during the coolest months (14% of days in 2004), and these trajectories are frequently associated with a European origin (Querol et al. 2000). Finally, if the air mass passing over Cartagena has a Mediterranean origin (2% of days in 2004), the resulting meteorological instability often ends in precipitation if the squalls are centred on the Gulf of Cadiz (Capel Molina 1986).

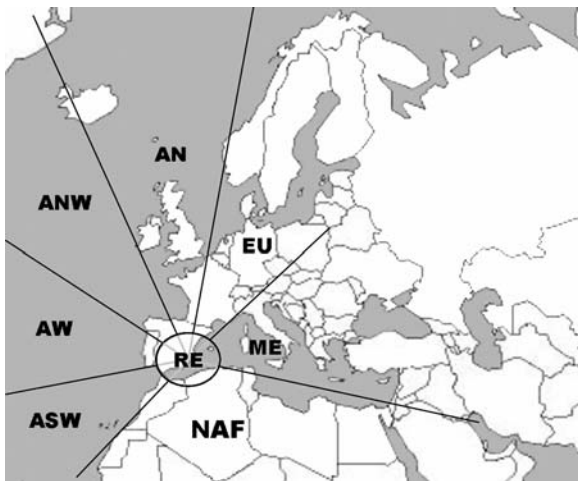


Fig. 2 Defined sectors for the air masses origin. *AN* Northern Atlantic, *ANW* Northwestern Atlantic, *AW* Western Atlantic, *ASW* Southwestern Atlantic, *NAF* Northern African, *ME* Mediterranean, *EU* European, *RE* Regional

Additional information describing these scenarios can be obtained from:

1. Dust Regional Atmospheric Modelling (DREAM; Nickovic et al. 2001), which offers a simulation of the advections of the African dust aerosol at a surface level.
2. SKIRON Forecast System (Kallos et al. 1997), which simulates the vertical integrated dust load.
3. Maps of total optical depth for sulphate, dust, and smoke; as well as maps of sulphate mass, dust and smoke (NRL 2003).
4. SeaWIFS-NASA Project (McClain et al. 1998), which offers satellite images.

The conjunction of the cited maps together with the chemical analysis of the PM filters builds the background for the full characterisation of pollution episodes in Cartagena.

3 Results and Discussion

3.1 PM Levels

Tables 1 and 2 show the levels of PM measured at the two stations. The mean PM₁₀ level at Bastarreche was $47 \mu\text{g m}^{-3}$ for the 98 days sampled with 45 of the days registered levels above $50 \mu\text{g m}^{-3}$. On the other hand, the mean PM_{2.5} level at Santa Ana was $22 \mu\text{g m}^{-3}$ suggesting that Santa Ana is in the usual range for Spanish urban background stations (Querol et al. 2004b). Only ten of the days sampled registered PM_{2.5} greater than $35 \mu\text{g m}^{-3}$. The thresholds discussed here are given by the Council Directive 1999/30/EC of 22 April 1999 and the recommendations from CAFE (2004).

The seasonality of PM levels, as well as the concentration of chemical species through the year, is the consequence of the combination of meteorological history, emission sources and African dust contributions. For example, Fig. 3 shows the concordance between a number of PM peaks and African Dust Outbreaks (ADO). This is consistent with the observation that 36% of days having PM₁₀ levels $>50 \mu\text{g m}^{-3}$ coincided with African trajectories. As expected (Fig. 4a), under these conditions, the mineral portion is highest ($20 \mu\text{g PM}_{10} \text{ m}^{-3}$, 32%), followed by the Secondary Inorganic Compounds (SIC) frac-

Table 1 Composition of PM10 at Bastarreche station

Bastarreche PM10 (summary of 98 samples)											
Component	Mean	Min.	Max.		Mean	Min.	Max.		Mean	Min.	Max.
	$\mu\text{g m}^{-3}$				ng m^{-3}				ng m^{-3}		
PM10	47	19	87	Li	0.4	0.05	1.3	Cs	0.06	0.04	0.2
OM+EC	11.3	3.6	26.3	Be	0.06	0.04	0.1	Ba	16	3.9	78
SiO ₂	3.1	0.2	18.0	P	28	1.9	61	La	0.3	0.02	1.6
CO ₃ ²⁻	3.5	0.5	8.6	Sc	0.10	0.04	0.5	Ce	0.7	0.1	3.2
Al ₂ O ₃	1.0	0.1	6.0	Ti	31	2.1	170	Pr	0.08	<0.01	0.4
Ca	1.8	0.3	4.7	V	11	0.9	47	Nd	0.3	<0.01	1.7
Fe	0.6	0.1	2.1	Cr	2.9	<0.01	44	Sm	0.08	<0.01	0.3
K	0.3	0.1	1.2	Mn	12	2.5	58	Eu	0.04	0.04	0.1
Na	0.8	0.1	2.8	Co	0.3	0.03	1.3	Gd	0.06	<0.01	0.3
Mg	0.3	<0.1	0.9	Ni	6.7	0.4	28	Tb	<0.01	<0.01	<0.1
SO ₄ ²⁻ marine	0.2	0.0	0.7	Cu	18	4.7	80	Dy	0.03	<0.01	0.1
SO ₄ ²⁻ nonmarine	5.1	1.4	12.1	Zn	504	64	3868	Ho	0.04	0.04	0.1
NO ₃ ⁻	2.7	0.1	8.4	Ga	0.2	0.05	0.9	Er	0.03	<0.01	0.1
Cl	0.5	<0.1	3.3	Ge	0.04	<0.01	0.8	Tm	<0.01	<0.01	<0.1
NH ₄ ⁺	1.3	<0.1	4.7	As	1.0	0.2	2.7	Yb	0.05	<0.01	0.2
				Se	0.6	0.04	2.8	Lu	<0.01	<0.01	<0.1
Mineral	10.7	1.4	39.4	Rb	0.9	0.2	4.2	Hf	0.3	<0.01	1.0
SIC	9.1	1.6	23.4	Sr	7.8	1.2	18	Ta	0.09	<0.01	1.5
OM+EC	11.3	3.6	26.3	Y	0.1	<0.01	0.6	W	0.07	<0.01	0.7
Marine	1.5	0.2	6.6	Zr	1.7	0.02	8.6	Tl	0.1	<0.01	2.8
Traces	0.7	0.2	4.2	Nb	0.1	<0.01	1.8	Pb	20	5.9	111
Undetermined	13.8	0.1	29.8	Mo	1.7	0.04	11	Bi	0.2	0.01	1.9
Total	33	13	69	Cd	0.7	0.06	10	Th	0.1	<0.01	0.5
% determined	71	49	100	Sn	2.0	0.3	4.9	U	0.2	<0.01	0.7
				Sb	3.4	0.9	8.0				

tion ($13 \mu\text{g PM}_{10} \text{ m}^{-3}$, 21%). Because this is a traffic oriented station, OM+EC ($11 \mu\text{g PM}_{10} \text{ m}^{-3}$, 18%) is the third major fraction. This increase of SIC has previously been observed in the Canary Islands during dust outbreaks and could be the result of the interaction of gas species like NO_x, HNO₃, SO₂ or H₂SO₄ with the African mineral dust, particularly CaCO₃, leading to accelerated gas to particulate conversion (Alastuey et al. 2005). The remaining 64% of days with PM10 levels $>50 \mu\text{g m}^{-3}$ (Fig. 4b) are associated with local/regional sources including traffic as OM+EC ($15 \mu\text{g PM}_{10} \text{ m}^{-3}$, 26%), followed by SIC ($11 \mu\text{g PM}_{10} \text{ m}^{-3}$, 19%) and the mineral fraction ($11 \mu\text{g PM}_{10} \text{ m}^{-3}$, 19%). This description would be consistent with motor vehicle exhaust, the abrasion of tires and breaks, and the resuspension of crustal materials on road pavement (Sternbeck et al. 2002; Wählín et al. 2006). As previously established, the mineral fraction in days without ADO could also

be increased because of the resuspension from road pavement as well as the resuspension of mineral materials on a regional-scale from non-vehicular sources.

3.2 Chemical Composition

The chemical fractions were defined as mineral, SIC, OM+EC, marine aerosol and trace components. On average, the non-allocated portion varied from 29% PM10 at Bastarreche to 34% PM2.5 at Santa Ana station, somehow slightly higher values to those described elsewhere (Querol et al. 2001b; Viana et al. 2002). This could be attributed to the increased relative humidity during the sampling and the presence of organic components from natural sources, such as amino-acids or humid substances detected in coastal rainwaters (Kieber et al. 2005), or from local anthropogenic sources including petrochemical and

Table 2 Composition of PM_{2.5} at Santa Ana station

Santa Ana PM _{2.5} (summary of 98 samples)											
Component	Mean	Min.	Max.		Mean	Min.	Max.		Mean	Min.	Max.
	μg m ⁻³				ng m ⁻³				ng m ⁻³		
PM _{2.5}	22	7	47	Li	0.3	0.01	4.5	Cs	0.01	<0.01	0.2
OM+EC	4.0	0.5	11.2	Be	0.01	<0.01	0.08	Ba	3.4	0.01	56
SiO ₂	1.0	0.05	8.4	P	9.8	0.5	33	La	0.1	0.01	0.7
CO ₃ ²⁻	0.9	0.02	3.1	Sc	0.1	<0.01	1.0	Ce	0.2	<0.01	1.4
Al ₂ O ₃	0.3	0.02	2.8	Ti	11	1.0	81	Pr	0.03	<0.01	0.1
Ca	0.4	0.01	1.5	V	6.0	0.05	29	Nd	0.09	<0.01	0.6
Fe	0.1	0.01	0.8	Cr	1.3	0.02	19	Sm	0.02	<0.01	0.1
K	0.2	0.03	0.7	Mn	2.7	0.08	14	Eu	<0.01	<0.01	0.02
Na	0.1	0.01	1.0	Co	0.1	<0.01	0.4	Gd	0.03	<0.01	0.1
Mg	0.1	<0.01	0.5	Ni	3.4	0.2	16	Tb	<0.01	<0.01	0.01
SO ₄ ²⁻ marine	0.04	<0.01	0.3	Cu	3.3	0.3	32	Dy	0.02	<0.01	0.2
SO ₄ ²⁻ nonmarine	3.5	0.6	10.2	Zn	13	0.09	186	Ho	<0.01	<0.01	0.01
NO ₃ ⁻	1.7	0.3	7.2	Ga	0.1	<0.01	0.4	Er	0.01	<0.01	0.1
Cl	0.4	0.1	0.8	Ge	0.1	0.01	0.5	Tm	<0.01	<0.01	0.01
NH ₄ ⁺	1.9	0.1	11.6	As	0.3	0.02	0.9	Yb	0.01	<0.01	0.09
				Se	0.3	<0.01	1.6	Lu	<0.01	<0.01	<0.01
				Rb	0.4	0.1	1.8	Hf	0.6	<0.01	1.7
Mineral	3.1	0.1	17.6	Sr	1.6	0.06	8.5	Ta	0.01	<0.01	0.07
SIC	7.0	1.3	22.9	Y	0.1	0.01	0.4	W	0.02	<0.01	0.08
OM+EC	4.0	0.5	11.2	Zr	7.3	0.05	19	Tl	0.08	<0.01	4.1
Marine	0.6	0.1	1.8	Nb	0.1	<0.01	0.4	Pb	5.7	0.2	33
Traces	0.1	0.02	0.2	Mo	0.9	<0.01	14	Bi	0.05	<0.01	0.2
Undetermined	7.7	<0.1	22	Cd	0.2	<0.01	1.0	Th	0.04	<0.01	0.2
Total	15	4	33	Sn	1.4	0.02	6.2	U	0.03	<0.01	0.3
% determined	66	40	112	Sb	0.6	0.05	2.6				

plastic industries. Concerning the humidity, a negative correlation between the marine fraction and the determined mass was identified. The proposed interpretation is that because of the Mediterranean location of Cartagena, when marine aerosol loaded air masses

arrive in the city, they also carry elevated water content, and the percentage of mass determined decreases. The results presented in Tables 1 and 2 seem to agree with what could be expected from a traffic-oriented station, as the highest PM₁₀ compo-

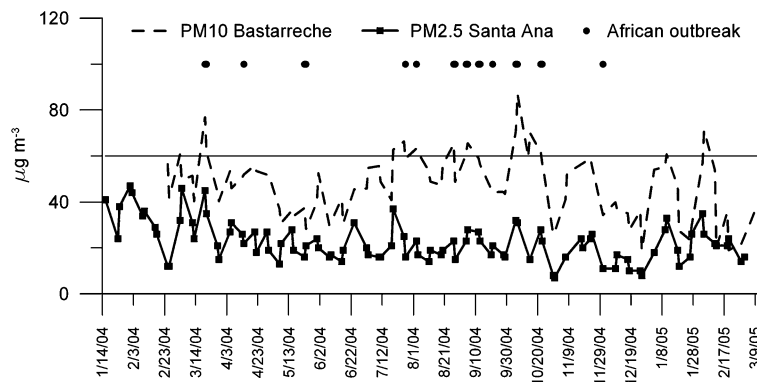


Fig. 3 Sequence of the mean daily levels of PM₁₀ at Bastarreche, PM_{2.5} at Santa Ana and those days when ADO were detected. The straight line points out that when more than 60 μg PM₁₀ m⁻³ were detected, there was coincidence with ADO

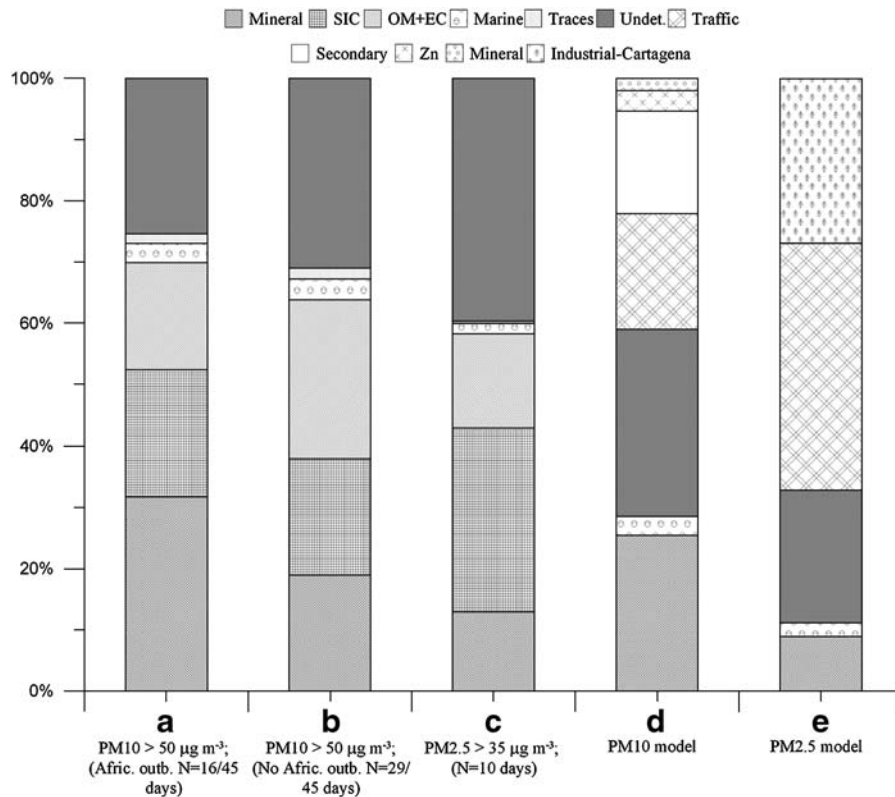


Fig. 4 Distribution of PM components: **a** when PM10 levels are above $50 \mu\text{g m}^{-3}$, during ADO; **b** when PM10 levels are above $50 \mu\text{g m}^{-3}$, when African dust was not present; **c** mean composition of PM2.5 during those days with higher levels than $35 \mu\text{g m}^{-3}$; **d** contribution of each identified source for

PM10 at Bastarreche; **e** contribution of each identified source for PM2.5 at Santa Ana. *Undet.* Non determined fraction; *Zn* the local Zn metallurgical industry; *Industrial-Cartagena* a blend of the industrial activity found in relationship with the secondary aerosol

ment is OM+EC ($11.3 \mu\text{g m}^{-3}$, 24%). On the other hand, the major component in PM2.5 is the SIC fraction ($7.0 \mu\text{g m}^{-3}$, 31%). For the ten days when the concentrations of PM2.5 aerosols were higher than $35 \mu\text{g m}^{-3}$ (Fig. 4c), there was a high non-determined fraction ($16.3 \mu\text{g m}^{-3}$, 40%), followed by SIC ($12.3 \mu\text{g m}^{-3}$, 30%) and OM+EC ($6.3 \mu\text{g m}^{-3}$, 15%). The levels of SIC during these days are noteworthy, and might be explained both by the recirculation of air masses in the Mediterranean basin (Querol et al. 2000; Millán et al. 2002) and by the oxidation of gaseous precursors emitted at a regional scale (Andreae et al. 2003; Perraudin et al. 2005).

3.3 PM Sources: Bastarreche and Santa Ana

Once FA was applied, six and five sources were determined at Bastarreche and Santa Ana, stations respectively. Tables 3 and 4 show the factor loadings of the principal species weighing in the factors (i.e. the

sources) and their percentage of variance explained by each factor. At the two stations, the mineral source explains the major variance; this source includes the natural minerals from ADO, the local/regional resuspension (Eltayeb et al. 2001; Querol et al. 2001a; Alastuey et al. 2005) and anthropogenic emissions coming from demolition and building. The traffic source is common at both of the stations as the second source that explains the largest fraction of the variance of the data. As expected, the highest component loadings in this factor are for OM+EC, Sb, NO_3^- . The marine source represents 5% and 7% of variance at Bastarreche and Santa Ana respectively, with Cl and Na as the main tracers in this factor. A factor interpreted as the local Zn metallurgy industry accounts for the 7% and 5% of variance at Bastarreche and Santa Ana respectively, with Zn, Cd and Pb as its markers, consistent with mineralogy and processing of sphalerite (del Valle Alonso et al. 1970). The secondary inorganic aerosols at Bastarreche account for 8% of variance,

Table 3 Results of the PCA for the PM10 fraction at Bastarreche

Factor 1		Factor 2		Factor 3		Factor 4		Factor 5		Factor 6	
Mineral		Traffic		Secondary		Zn		Marine		Shipyards	
Rb	0.95	Sn	0.92	NH ₄ ⁺	0.94	Cd	0.95	Cl	0.95	Cr	0.76
Mg	0.92	Sb	0.92	SO ₄ ²⁻	0.85	Zn	0.86	Na	0.81	Ni	0.67
Al ₂ O ₃	0.91	OM+EC	0.87	V	0.57	Pb	0.84	Mg	0.34	Co	0.40
Ti	0.91	Cu	0.67	NO ₃ ⁻	0.50	Mn	0.72			V	0.34
K	0.89	As	0.63	Ni	0.40	Cu	0.66			P	-0.29
Sr	0.88	NO ₃ ⁻	0.61			Fe	0.45				
Fe	0.81	P	0.54			As	0.34				
Co	0.80	Pb	0.39			OM+EC	0.32				
Ca	0.75	Ca	0.39								
Mn	0.63	Ba	0.32								
P	0.61	Zn	0.27								
Ba	0.61	Na	-0.36								
V	0.58										
Ni	0.53										
SO ₄ ²⁻	0.37										
As	0.30										
% Var.=40		% Var.=21		% Var.=8		% Var.=7		% Var.=5		% Var.=5	

Components with factor loadings between 0.25 and -0.25 are excluded and those ones with factor loadings >0.50 are in bold types. % Var. Percentage of variance explained by each factor, Zn the local Zn metallurgical industry

with SO₄²⁻, NO₃⁻, NH₄⁺ as main tracers. A mixture of compounds appear clustered at Santa Ana, which might represent aged air masses containing the emissions from the local industries next to the city centre (SO₄²⁻, V, Ni, As, NH₄⁺). Finally, the last factor at Bastarreche is the one identified as the military shipyard (5% of variance) with Cr and Ni as main tracers.

Once the sources have been identified, their daily contribution to the total aerosol mass was calculated using MLRA. Based on this analysis, Fig. 4d and e show each mass contribution of individual sources to the total levels of PM.

In summary, the association among sources and the chemicals that they emit are presented in Tables 5 and 6:

Table 4 Results of the PCA for the PM2.5 fraction at Santa Ana

Factor 1		Factor 2		Factor 3		Factor 4		Factor 5	
Mineral		Traffic		Ind.-Cartagena		Marine		Zn	
Ti	0.95	OM+EC	0.88	SO ₄ ²⁻	0.84	Na	0.78	Zn	0.87
Fe	0.94	NO ₃ ⁻	0.83	V	0.81	Cl	0.56	Pb	0.34
Al ₂ O ₃	0.94	Cl	0.62	Ni	0.71	Pb	0.38		
Mn	0.91	Sb	0.60	As	0.69	OM+EC	-0.26		
Rb	0.85	K	0.54	NH ₄ ⁺	0.67	Ca	-0.36		
K	0.71	Pb	0.43	Pb	0.46				
Ca	0.64	As	0.37	NO ₃ ⁻	0.34				
Ni	0.41	NH ₄ ⁺	0.36	Mg	0.30				
Na	0.38	Mg	-0.54						
V	0.38								
Mg	0.37								
% Var.=35		% Var.=19		% Var.=10		% Var.=7		% Var.=5	

Components with factor loadings between 0.25 and -0.25 are excluded and those ones with factor loadings >0.50 are in bold types. % Var. Percentage of variance explained by each factor, Ind.-Cartagena a mixture of the industries from the city, Zn the local Zn metallurgical industry

Table 5 Percentage contribution from each identified factor to the chemical species analysed in PM10

Percent	Mineral	Traffic	Secondary	Zn	Marine	Shipyard	% Det.
OM+EC	6	82		10			98
Al ₂ O ₃	92		11				103
Ca	51	31		5		11	98
Fe	60	22	4	16			102
K	64	24	9	5			102
Na	13		5		71	9	98
Mg	68		4	3	23		98
SO ₄ ²⁻	29		59	2	7	9	106
NO ₃ ⁻		71	30	5			106
Cl		20		3	79		102
NH ₄ ⁺	11		94	2			107
P	34	41	10			21	106
Ti	88		12	3			103
V	49		43				92
Cr	45	20	10	2			77
Mn	51	18		31			100
Co	67	5	14	3	3		92
Ni	48	4	32				84
Cu	8	65		24			97
Zn	6	45		42			93
As	28	57	7	9			101
Rb	90		11				101
Sr	56	13	6	2	6	18	101
Cd				85		26	111
Sn	3	84	3	7			97
Sb	8	86		6			100
Pb	10	42	8	37		10	107

% Det. Total recovery through the addition of every source, Zn the local Zn metallurgical industry

There is general agreement between the type of source and their expected composition (Canadian Chemical Producers' Association 2001). Two specific sources in Cartagena are the Zn metallurgy and the military shipyard. The first one is characterised by Zn in the smallest size fraction and Cd, Zn and Pb in the coarsest size. The emissions from the shipyard are only detected in the nearest station to the harbour (i.e. Bastarreche). The shipyard slightly contributes to Cd, Sr and P although, as established in Table 5, its main tracers were Cr and Ni (U.S. Department of Navy 1996).

3.4 Characterization of ADO

The identification of ADO was performed according to Querol et al. (2004a). However, no different factor for these ADO was distinguished from the mineral fraction in PCA (Tables 3 and 4). To better establish if the chemical species are carried in the African dust or

they are indigenous in Cartagena, we propose the ratio of each chemical species divided by the total mass of the crustal compounds in days under the influence of ADO and days with no ADO (Table 7). In this way, those chemical elements (e.g. Al₂O₃, Ti, Rb) whose mean of the ratios in days with ADO was statistically higher (level of significance < 0.001) than mean of the ratios in days without ADO could be used as tracers of the influence of the African events. Conversely, those chemical elements (e.g. Ca, Cu, Pb) whose mean of the ratios in days with ADO was statistically lower (level of significance < 0.001) than mean of the ratios in days without ADO could be used as tracers of the local aerosol influence in Cartagena: in other words, in ADO days those elements with the mentioned decreased ratio would experiment a dilution by the African dust. The results presented in Table 7 are in agreement with the bibliography for African tracers (Salvador et al.

Table 6 Percentage contribution from every identified factor to the chemical species analysed in PM2.5

Percent	Mineral	Traffic	Ind.-Cartagena	Marine	Zn	% Det.
OM+EC		85	6		7	98
Al ₂ O ₃	91		18			109
Ca	49	20	22			91
Fe	87		20			107
K	40	54			10	104
Na	9			95		104
Mg	22		45	29		96
SO ₄ ²⁻	5		66	18	15	104
NO ₃		84	17			101
Cl		26	6	60	6	98
NH ₄ ⁺		47	52			99
Ti	91		15			106
V	29		77			106
Mn	78		25			103
Ni	27		80			107
Zn					111	111
As	10	31	41	10	12	104
Rb	67	17	20			104
Sb	11	96				107
Pb		32	37	17	22	108

% Det. Total recovery through the addition of every source, *Ind.-Cartagena* factor acting as a mixture of the industries from the city, *Zn* the local Zn metallurgical industry

Table 7 Significant differences (level of significance < 0,001) in the ratio “mass of each chemical species divided by the total mass of mineral fraction” found in days with ADO

Chemical species	PM10	PM2.5
OM+EC	D	
SiO ₂	I	I
CO ₃ ²⁻	D	
Al ₂ O ₃	I	I
Ca	D	
Ti	I	
Cu	D	
Rb	I	
Nb	I	
Sb	D	
La	I	
Ce	I	
Nd	I	
Ho	D	
Pb	D	

The blanks mean that no significant differences were found.

D Decrease, I Increase

2004; Viana et al. 2006) and the elemental composition in local soils [i.e. Cu and Pb occur notoriously in local soils (Moreno-Grau et al. 2002)].

4 Conclusions

Chemical composition of PM10 and PM2.5 was determined at a traffic hotspot and a suburban location in the Southeast of the Iberian Peninsula. A Factor Analysis allowed us to observe the following PM sources: crustal, traffic, secondary, marine, Zn metallurgy industry and shipyard. The crustal source includes local dust resuspension, ADO and road dust resuspension. The secondary aerosols source represents aged air masses (i.e. NH₄⁺, SO₄²⁻, NO₃⁻) together with the contributions from the power station (V, Ni). A Zn metallurgical industry source was described by Cd, Zn and Pb in the two grain sizes. Finally, a source from a shipyard had a minimal contribution, was detected only in the coarser fraction, and was described by Cr and Ni. In the cases when the city is under environmental conditions which increase the PM levels because of natural causes, the clear definition of the reasons (i.e. anthropogenic or natural)

of high PM levels were identified based on isentropic back-trajectory air masses and aerosol maps.

Acknowledgements This study was supported by research projects from the D.G. Environmental Quality and Assessment from the Spanish Ministry of the Environment and the Plan Nacional de I+D from the Spanish Ministry of Education and Science (CGL2004-05984_C07-02/CLI, REN2001-0659-C03-03, REN2003-01997). Financial support was also provided by the Spanish Ministry of Education and Science through a “FPU” grant to Luis Negral.

References

- Alastuey, A., Querol, X., Castillo, S., Escudero, M., Ávila, A., Cuevas, E., et al. (2005). Characterisation of TSP and PM_{2.5} at Izaña and Sta. Cruz de Tenerife (Canary Islands, Spain) during a Saharan Dust Episode (July 2002). *Atmospheric Environment*, *39*, 4715–4728.
- Andreae, M. O., Andreae, T. W., Meyerdierks, D., & Thiel, C. (2003). Marine sulfur cycling and the atmospheric aerosol over the springtime North Atlantic. *Chemosphere*, *52*, 1321–1343.
- Bates, T. S., Quinn, P. K., Coffman, D. J., Jonson, J. E., & Middlebrook, A. M. (2005). Dominance of organic aerosols in the marine boundary layer over the Gulf of Maine during NEAQS 2002 and their role in aerosol light Scattering. *Journal of Geophysical Research*, *110*, (D18202).
- CAFE (Clean Air for Europe). (2004). Second Position Paper on PM, CAFE Programme. (European Comisión).
- Canadian Chemical Producers' Association. (2001). *Ambient particulate matter characterization guidelines*. Ottawa: Canadian Chemical Producers' Association.
- Capel Molina, J. J. (1986). El clima del territorio de Cartagena. In J. Mas García (Ed.) *Historia de Cartagena. Tomo I* (pp. 171–192). Murcia: Ediciones Mediterráneo.
- Cirera, L. (2005). Evaluación del plan operativo de intervención industrial sobre las emisiones atmosféricas de las fábricas urbanas y sus efectos en la morbimortalidad de Cartagena. Dissertation, University of Murcia.
- Consejería de Sanidad de la Región de Murcia (1991). Contaminación atmosférica y salud en Cartagena. Monografías Sanitarias 10. (Cartagena).
- Del Valle Alonso, J. L., Fernandez de Palencia y Roc, A., Rovira Pereira, A., Moreno Clavel, J., & Guzman Jiménez, R. (1970). Treatment of the leaching residues at the electrolytic zinc plant of Espanola del Zinc, S.A.. In C. H. Cotterill, & J. M. Cigan (Eds.) *AIME World symposium on mining & metallurgy of lead & zinc, vol. II* (pp. 348–388). New York: The American Institute of Mining, Metallurgical, and Petroleum Engineers.
- Draxler, R. R., & Hess, G. D. (2004). Description of the HYSPLIT 4 modelling system. Retrieved March 2, 2005 from NOAA technical memorandum, ERL ARL-224 Web site: <http://www.arl.noaa.gov/ready/hysplit4.html>.
- Eltayeb, M. A. H., Injuk, J., Maenhaut, W., & Van Grieten, R. E. (2001). Elemental composition of mineral aerosol generated from Sudan Sahara sand. *Journal of Atmospheric Chemistry*, *40*, 247–273.
- EPA (Environmental Protection Agency). (2006). 40 CFR Parts 53 and 58, Revisions to Ambient Air Monitoring Regulations, Final Rule. Retrieved November 20, 2006 from EPA Web site: <http://www.epa.gov/ttn/amtic/files/ambient/pm25/pt535806.pdf>.
- Gangoiti, G., Millán, M. M., Salvador, R., & Mantilla, E. (2001). Long-range transport and re-circulation of pollutants in the western Mediterranean during the project Regional Cycles of Air Pollution in the West-Central Mediterranean Area. *Atmospheric Environment*, *35*, 6267–6276.
- Harrison, R. M., Smith, D. J. T., & Luhana, L. (1996). Source apportionment of atmospheric polycyclic aromatic hydrocarbons collected from an urban location in Birmingham, U. K. *Environmental Science and Technology*, *30*, 825–832.
- Hopke, P. K. (1992). Factor and correlation analysis of multivariate environmental data. In C. N. Hewitt (Ed.) *Methods of environmental data analysis* (pp. 139–180). England: Elsevier Science.
- Kallos, G., Kotroni, V., & Lagouvardos, K. (1997). *The regional weather forecasting system SKIRON: An overview*. Proceedings of the symposium on regional weather prediction on parallel computer environments, Retrieved February 23, 2004 from University of Athens Web site: <http://forecast.uoa.gr/dustindx.html>.
- Kieber, R. J., Long, M. S., & Willey, J. D. (2005). Factors influencing nitrogen speciation in coastal rainwater. *Journal of Atmospheric Chemistry*, *52*, 81–99.
- Künzli, N., Mudway, I. S., Götschi, T., Shi, T., Kelly, F. J., Cook, S., et al. (2005). Comparison of oxidative properties, light absorbance, total and elemental mass concentration of ambient PM_{2.5} collected at 20 European sites. *Environmental Health Perspectives*, *114*, 684–690.
- Li, A., Jang, J. K., & Scheff, P. A. (2003). Application of EPA CMB8.2 Model for source apportionment of sediment PAHs in Lake Calumet, Chicago. *Environmental Science and Technology*, *37*, 2958–2965.
- Martínez García, M. J., Moreno-Grau, S., Martínez García, J. J., Moreno, J., Bayo, J., Guillén Pérez, J. J., et al. (2001). Distribution of the metals lead, cadmium, copper, and zinc in the top soil of Cartagena, Spain. *Water, Air, and Soil Pollution*, *131*, 329–347.
- McClain, C. R., Cleave, M. L., Feldman, G. C., Gregg, W. W., Hooker, S. B., & Kuring, N. (1998). Science quality SeaWiFS data for global biosphere research. *Sea Technology*, *39*, 10–16.
- Millán, M. M., Sanz, M. J., Salvador, R., & Mantilla, E. (2002). Atmospheric dynamics and ozone cycles related to nitrogen deposition in the western Mediterranean. *Environmental Pollution*, *118*, 167–186.
- Molnár, A., & Mészáros, E. (2001). On the relation between the size and chemical composition of aerosol particles and their optical properties. *Atmospheric Environment*, *35*, 5053–5058.
- Moreno-Grau, S. (2006). *La vigilancia de la contaminación atmosférica: Pasado, presente y futuro*. Cartagena: Academia de Farmacia Santa María de España de la Región de Murcia.
- Moreno-Grau, S., Cascales-Pujalte, J. A., Martínez-García, M. J., Angosto, J. M., Moreno, J., Bayo, J., et al. (2002). Relationships between levels of lead, cadmium, zinc, and

- copper in soil and settleable particulate matter in Cartagena (Spain). *Water, Air, and Soil Pollution*, 137, 365–383.
- Nickovic, S., Kallos, G., Papadopoulos, A., & Kakaliagou, O. (2001). A model for prediction of desert dust cycle in the atmosphere. *Journal of Geophysical Research*, 106, 18113–18129.
- NRL (Naval Research Laboratory). (2003). Naval aerosol analysis and prediction systems, global aerosol model. Retrieved March 7, 2005 from NRL Web site: http://www.nrlmry.navy.mil/aerosol/index_shortcuts.html.
- Pacyna, J. M. (1986). Emission factors of atmospheric elements. In J. O. Nriagu, & C. I. Davidson (Eds.) *Toxic metals in the atmosphere* (pp. 33–52). London: Wiley.
- Perraudin, E., Budzinski, H., & Villenave, E. (2005). Kinetic study of the reactions of NO₂ with polycyclic aromatic hydrocarbons adsorbed on silica particles. *Atmospheric Environment*, 39, 6557–6567.
- Querol, X., Alastuey, A., Chaves, A., Spiro, B., Plana, F., & Lopez-Soler, A. (2000). Sources of natural and anthropogenic sulphur around the Teruel power station, NE Spain. Inferences from sulphur isotope geochemistry. *Atmospheric Environment*, 34, 333–345.
- Querol, X., Alastuey, A., Rodríguez, S., Plana, F., Mantilla, E., & Ruiz, C. R. (2001b). Monitoring of PM10 and PM2.5 around primary anthropogenic emission sources. *Atmospheric Environment*, 35, 845–858.
- Querol, X., Alastuey, A., Rodríguez, S., Plana, F., Ruiz, C. R., Cots, N., et al. (2001a). PM10 and PM2.5 source apportionment in the Barcelona Metropolitan area, Catalonia, Spain. *Atmospheric Environment*, 35, 6407–6419.
- Querol, X., Alastuey, A., Rodríguez, S., Viana, M. M., Artiñano, B., Salvador, P., et al. (2004a). Levels of particulate matter in rural, urban and industrial sites in Spain. *Science of the Total Environment*, 334–335, 359–376.
- Querol, X., Alastuey, A., Viana, M. M., Rodríguez, S., Artiñano, B., Salvador, P., et al. (2004b). Speciation and origin of PM10 and PM2.5 in Spain. *Journal of Aerosol Science*, 35, 1151–1172.
- Reis, M. A., Oliveira, O. R., Alves, L. C., Rita, E. M. C., Rodríguez, F., Fialho, P., et al. (2002). Comparison of continental Portugal and Azores Islands aerosol during a Sahara dust storm. *Nuclear Instruments and Methods in Physics Research B*, 189, 272–278.
- Salvador, P., Artiñano, B., Alonso, D. G., Querol, X., & Alastuey, A. (2004). Identification and characterisation of sources of PM10 in Madrid (Spain) by statistical methods. *Atmospheric Environment*, 38, 435–447.
- Stembeck, J., Sjödin, A., & Andréasson, K. (2002). Metal emissions from road traffic and the influence of resuspension—results from two tunnel studies. *Atmospheric Environment*, 36, 4735–4744.
- Tanner, P. A., & Wong, A. Y. S. (2000). Soluble trace metals and major ionic species in the bulk deposition and atmosphere of Hong Kong. *Water, Air, and Soil Pollution*, 122, 261–279.
- Thurston, G. D., & Spengler, J. D. (1985). A quantitative assessment of source contributions to inhalable particulate matter pollution in Metropolitan Boston. *Atmospheric Environment*, 19, 9–25.
- Turpin, B. J., Saxena, P., & Andrews, E. (2000). Measuring and simulating particulate organics in the atmosphere: problems and prospects. *Atmospheric Environment*, 34, 2983–3013.
- US Department of the Navy. (1996). Impact of recent and anticipated changes in airborne emission exposure limits on shipyard workers. The National Shipbuilding Research Program. Report No. NSRP 0463.
- Viana, M., Querol, X., & Alastuey, A. (2006). Chemical characterisation of PM episodes in NE Spain. *Chemosphere*, 62, 947–956.
- Viana, M., Querol, X., Alastuey, A., Cuevas, E., & Rodríguez, S. (2002). Influence of African dust on the levels of atmospheric particulates in the Canary Islands air quality network. *Atmospheric Environment*, 36, 5861–5875.
- Wählin, P., Berkowicz, R., & Palmgren, F. (2006). Characterisation of traffic-generated particulate matter in Copenhagen. *Atmospheric Environment*, 40, 2151–2159.