

Source apportionment of fine and coarse particulate matter in a sub-urban area at the Western European Coast

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Abstract

Aerosol chemical composition data for $PM_{2.5}$ and $PM_{10-2.5}$, was acquired during the year 2001 at a sub-urban area located in the north outskirts of Lisbon. Principal component analysis (PCA) and multilinear regression analysis (MLRA) were used to identify possible sources of particulate matter (PM) and to determine their mass contribution. Seven main groups of sources were identified: soil, sea, secondary aerosols, road traffic, fuel-oil combustion, coal combustion and a Se/Hg emission source. In $PM_{2.5}$, secondary aerosol and vehicle exhaust contributed on average, with 25% and 22% to total mass, respectively, while sea spray and soil represented, respectively, 47% and 20% of the coarse fraction mass loading. Maritime air mass transport has a significant role on air quality in the North of Lisbon. Maritime transport scenarios are very frequent and promote the decrease of anthropogenic and mineral aerosol concentrations. The highest PM levels were recorded during South Continental episodes. These episodes are characterized by high mineral aerosol contents, due to the transport of dust from the interior of Iberian Peninsula and the Sahara desert.

After identifying the contribution of PM sources, it is possible to conclude that abatement strategies to improve local air quality should focus on traffic and on non-mobile combustion processes emitting sulphur and NO_x , which conduce to the formation of secondary aerosols.

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1. Introduction

Urban and sub-urban areas contain a large concentration of people and anthropogenic industrial and traffic activities. Therefore, they exhibit both the highest levels of pollution and the largest targets of impact. Several reports revealed significant correlations between

particulate matter (PM) levels and increased respiratory and cardiovascular diseases, and mortality (Pope et al., 2002). Understanding and controlling air pollution in these areas is then important but difficult, mainly for particulate pollutants that have a mixture of primary and secondary sources. Emission inventories and transport models are problematic in the evaluation of particulate atmospheric pollution because important sources are frequently fugitive. Moreover, there is an important contribution of secondary particles for the aerosol and the gas-particle transformation models are not always reliable. The study of particle concentrations

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at the receptor is essential to elucidate the sources of the aerosols and the processes associated with their formation. Abatement strategies may significantly improve the air quality after identifying the main PM sources.

In South European regions, such as Portugal, in addition to anthropogenic sources, the ambient aerosol has an important contribution from natural dust, due to local emissions from bare soil, and an influence of episodic African dust transport outbreaks (Artiñano et al., 2001). Moreover, the Portuguese coastal areas have an important input of marine aerosol (Pio et al., 1996). This is due to the geographic position of Portugal (on the extreme southwest of Europe) and the dominant western wind regime, influenced by the presence of the semi-permanent Azores high-pressure and the Icelandic low-pressure systems over the North Atlantic Ocean.

The present study uses the measurements of particulate air quality level in the sub-urban region of Great Lisbon to evaluate the importance of different sources and processes responsible for the high degree of particulate atmospheric contamination observed frequently in sub-urban areas of large urban conurbations. It is important to understand, how sources, which are directly accessible to the local authorities, contribute to the PM₁₀ pollution and what sort of additional actions should be taken at regional, national, EC and worldwide levels to control particulate air pollution. For that, an association of complementary tools was applied, including: Principal component analysis (PCA), multilinear regression analysis (MLRA), enrichment factors, air mass back trajectories analyses, meteorological data and particle size distribution.

2. Experimental

2.1. Site description

During 2001, PM was sampled in Bobadela, a sub-urban and industrial area in the outskirts of Lisbon (latitude 38°48'50"N, longitude 9°05'29"W and height 15 m). The sampling station was located 10 km northeast from the urban centre of Lisbon, being surrounded by high density traffic roads (1 km from a motorway and 10 m from a main road) by industrial activities including an urban waste incinerator (3 km), a fuel oil power station (30 km), a cement factory (20 km) and several chemical, food and glass factories. Bobadela is located on the right side of the Tagus Estuary valley, approximately 20 km from the Atlantic Ocean (Fig. 1b and c).

2.2. Description of the sampling equipment

A total of 104 PM samples were collected twice a week, during 24 h periods. Sampling was done with one low volume and one high volume samplers, which

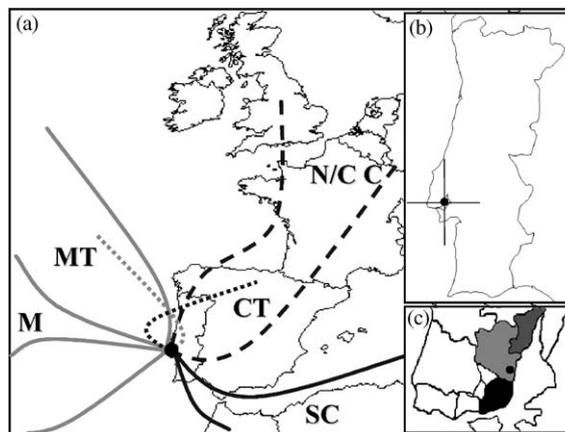


Fig. 1. Sampling site localization (●) (a) in Europe with air mass categorization, based on 4 day backward trajectories obtained from Hysplit model. M—maritime; MT—maritime transformed; SC—South Continental; N/C C—north/centre Continental; CT—Continental transformed; (b) in Portugal; and (c) in Lisbon and outskirts (Black pattern—urban centre of Lisbon. Light and dark grey patterns—Loures and Vila Franca de Xira sub-urban/industrial areas on the right margin of the Tagus Estuary, concentrating the Lisbon industrial congregate).

operated side by side. The low volume sampler (Gent PM₁₀ sampler) was equipped with a stacked filter unit, which carried, in two sequential stages, 47 mm Nuclepore polycarbonate filters, with 8 and 0.4 μm pore size. Upstream of the coarse filter was located a pre-impactor stage. The air was sampled at a rate of 15–16 l min⁻¹, which allowed the collection of coarse particles with aerodynamic diameters (AD) between 10 and 2.5 μm, in the first stage, and fine particles with AD < 2.5 μm in the second stage (Maenhaut, 1992).

The high volume sampler was equipped with a Sierra PM₁₀ size selective inlet and a Sierra single stage impactor plate to separate particles in two size fractions: 2.5 μm < AD < 10 μm and AD < 2.5 μm. This sampler operated at a flow rate of 1.13 m³ min⁻¹. High Vol. aerosol samples were collected on pre-washed and thermally treated Whatman QM-A quartz fibre filters (Tanner et al., 1979).

2.3. Gravimetric and chemical analysis

The filter loads were measured by gravimetry in a controlled clean room (class 10,000). Nuclepore filters were weighted on a semi-micro-balance and quartz filters on a micro-balance. Filter weight before and after sampling was obtained as the average of three measurements, when observed variations were less than 5%.

Samples collected in Nuclepore filters were used for elemental analysis. The exposed filters were cut into three parts of different sizes: half was analyzed by

Instrumental Neutron Activation Analysis (INAA) (Bowen and Gibbons, 1963) with the k_0 methodology (De Corte, 1987); a quarter was analyzed by Particle Induced X-Ray Emission (PIXE) (Johansson and Campbell, 1988); the remaining filter quarter was kept in storage for other possible measurements or replicates.

Previous to the sampling campaign, tests of reproducibility within the filters and between filters were taken, using parallel sampling with two similar sampling units and measuring the particle species by INAA and PIXE. Results were reproducible to within 5–15%, providing strong support for the validity of the analytical techniques. The details of sampling and analytical control tests are given in Almeida (2004) and Almeida et al. (2003a, b). The accuracy of analytical methods was evaluated with NIST filter standards, revealing results with an agreement of $\pm 10\%$ (Almeida, 2004; Freitas et al., 2005).

Exposed quartz fibre filters were used for the determination of water-soluble inorganic ions and for measurement of black carbon (BC) and organic carbon (OC) content. For water-soluble ions determination, one portion of the filter was extracted with distilled deionized water by ultrasonic and mechanical shaking and filtered through a pre-washed Whatman 42 filter. The aqueous extract was analyzed by ion chromatography (Chow and Watson, 1999) (Cl^- , NO_3^- and SO_4^{2-}), indophenol-blue spectrophotometry (Weatherburn, 1967) (NH_4^+), atomic absorption spectroscopy (Grohse, 1999) (Ca^+ , Mg^{2+} , Na^+ and K^+) and potentiometry (H^+).

BC and OC contents were determined in another portion of the quartz fibre filters with a thermo-optical system, based on the thermal desorption/oxidation to CO_2 with subsequent determination by non-dispersive infrared spectrophotometry (Pio et al., 1993). Because of lack of time, not all samples collected were analyzed for BC and OC.

Blank Nuclepore and quartz filters were treated the same way as regular samples. All measured species were very homogeneously distributed; therefore concentrations were corrected by subtracting the filter blank contents.

2.4. Air mass back trajectories

Four days backward trajectories, ending in Bobadela, at the starting sampling time and at 50 m height, were calculated with the Hysplit Model (Draxler, 1994) using the vertical velocity option. According to the backward trajectories, air masses arriving at Bobadela during the sampling campaign were classified into five main groups (see Fig. 1a): M—maritime air masses—if backward trajectories indicate an ocean origin, without continental contamination, during the previous 4 days; MT—maritime transformed air masses—if backward

trajectories indicate an ocean origin, with a final re-circulation through the Iberian peninsula; SC—South Continental air masses—if backward trajectories indicate an African or southern Europe origin, N/CC—North/centre Continental air masses—if backward trajectories indicate an origin in the North or centre of Europe; and CT—Continental transformed air masses—if backward trajectories indicate an European origin with a final re-circulation through the ocean. Only 2 days associated with Continental transformed air masses were identified, therefore this air mass back trajectory will not be considered. Other two samples could not be included in none of the categories established before.

2.5. PCA and MLRA procedures

Sources categories for $\text{PM}_{2.5}$ and $\text{PM}_{10-2.5}$ constituents were identified by means of principal component factor analysis (PCA) using STATISTICA software. This was performed by utilising the orthogonal transformation method with Varimax rotation and retention of principal components whose eigenvalues were greater than unity. Factor loadings indicate the correlation of each pollutant species with each component and are related to the source emission composition.

Only the species quantified in more than 80% of the samples, both in fine and coarse fraction were retained for PCA analysis. For data below detection limit, half of the detection limit values were used for calculations. PCA was performed with and without samples with outliers. The conclusions obtained were identical, therefore all samples were considered.

The contribution of each source group to the aerosol burden was then quantitatively assessed by means of MLRA. MLRA was applied to the experimental data, using as dependent variables $\text{PM}_{2.5}$ and $\text{PM}_{10-2.5}$ total mass concentrations and as independent variables the principal component factor scores. As the factor scores obtained from the PCA are normalized, with mean zero and standard deviation equal to unity, the true zero for each factor score was calculated by introducing an artificial sample with concentrations equal to zero for all variables. PCA was performed and the factor scores obtained for this artificial sample subtracted from the factor scores of each one of the other samples (Thurston and Spengler, 1985).

3. Results and discussion

The annual average levels of total mass and trace constituents are summarized in Table 1. Table 1 also contains average fine/coarse ratio and information concerning the level of atmospheric concentrations, stratified by the origin of sampled air mass.

Table 1
Summary of aerosol average concentration at Bobadela (values in ng m^{-3})

	PM _{2.5}					PM _{10-2.5}					PM _{2.5} / PM _{10-2.5}
	All (n = 104)	M (n = 47)	MT (n = 16)	SC (n = 17)	N/CC (n = 20)	All (n = 104)	M (n = 47)	MT (n = 16)	SC (n = 17)	N/CC (n = 20)	All (n = 104)
Total	24,000	14,000	22,000	30,000	29,000	16,000	14,000	12,000	17,000	13,000	1.0
Al	77	27	64	110	61	180	66	170	290	140	0.45
Si	200	68	190	270	170	470	180	390	770	400	0.49
K	120	47	110	180	150	150	100	120	200	140	0.96
Ca	230	120	240	200	210	1100	580	830	1400	1100	0.38
Sc	0.013	0.0038	0.0084	0.018	0.010	0.048	0.014	0.036	0.074	0.040	0.30
Ti	8.5	4.2	8.1	8.6	6.1	21	10	16	29	18	0.42
V	6.7	3.5	5.7	9.7	7.0	4.5	2.8	2.5	5.1	3.8	2.1
Mn	2.3	1.2	2.6	3.2	2.4	4.2	2.0	3.7	6.5	4.1	0.66
Fe	120	58	110	200	120	280	130	220	460	250	0.51
Co	0.087	0.042	0.077	0.12	0.094	0.12	0.044	0.085	0.19	0.12	1.0
Ni	2.6	1.5	2.5	3.5	2.7	1.6	0.73	1.0	2.4	1.6	2.4
Cu	5.4	2.9	4.5	7.3	5.5	5.7	2.8	3.9	9.1	5.1	1.2
Zn	18	6.3	15	23	16	18	6.9	14	26	14	1.2
As	0.31	0.087	0.25	0.36	0.41	0.16	0.048	0.086	0.18	0.13	4.0
Se	0.51	0.30	0.74	0.86	1.3	0.2	0.14	0.19	0.36	0.53	3.8
Br	3.0	2.0	3.1	2.6	3.1	1.2	1.1	0.75	1.1	1.3	4.0
Sb	1.5	0.70	1.3	1.6	1.7	1.1	0.53	0.77	1.7	1.1	1.6
La	0.067	0.029	0.057	0.10	0.068	0.17	0.062	0.14	0.28	0.17	0.46
Sm	0.011	0.0037	0.0083	0.013	0.0086	0.031	0.011	0.025	0.046	0.031	0.37
Hg	0.061	0.061	0.074	0.067		0.066	0.067	0.068	0.068	0.086	1.4
Pb	8.6	4.1	9.0	11	8.5	6.0	2.6	4.4	7.4	3.5	2.6
SO ₄ ²⁻	3900	1900	5200	4300	3900	480	520	440	490	400	7.6
NO ₃ ⁻	1300	650	780	1700	1700	1000	510	1200	1100	990	2.0
Cl ⁻	250	400	140	190	170	1400	1800	530	440	450	0.65
NH ₄ ⁺	1300	330	1500	1600	1500	16	6.4	11	10	20	110
Na ⁺	400	430	300	170	210	990	1200	530	320	350	0.53
K ⁺	130	49	100	190	160	43	45	35	38	32	3.9
Mg ²⁺	52	54	40	34	32	110	130	70	52	56	0.61
Ca ²⁺	380	220	390	400	373	430	330	420	510	440	0.90
OC	4300	2200	3400	5300	6100	920	1000	800	1300	860	4.3
BC	1500	1100	1100	1500	1600	39	11	37	38	37	170

M—maritime; MT—maritime transformed; SC—South Continental; N/CC—North/centre Continental. Ratio between fine and coarse fraction.

Average PM_{2.5} mass concentration at Bobadela is $24 \mu\text{g m}^{-3}$. These levels are mainly due to anthropogenic particles providing from local sources and from long-range transport. Maritime trajectories presented lower PM_{2.5} concentrations due to the transport of clean air masses from the Atlantic Ocean.

Average PM_{10-2.5} mass concentration at Bobadela is $16 \mu\text{g m}^{-3}$. PM_{10-2.5} reaches higher concentrations for maritime trajectories, which transport coarse particles from the sea, and South Continental trajectories, which

transport mineral particles from North of Africa and South of Europe.

PM₁₀ average concentration ($40 \mu\text{g m}^{-3}$) is above the EU annual PM₁₀ standard of $20 \mu\text{g m}^{-3}$ target for 2010. The EU 24 h PM₁₀ limit value of $50 \mu\text{g m}^{-3}$ was exceeded more than 19 times (in 104 sampling days). Legislation target is 7 days exceedances per year, for 2010. In Lisbon, the PM_{2.5}/PM₁₀ ratio is lower than in other sub-urban European areas (Van Dingenen et al., 2004). Apart from anthropogenic sources, PM₁₀ is

considerably influenced by coarse particles with marine and mineral origin. Consequently, PM_{2.5} would be a better choice to evaluate the negative impact of anthropogenic activities on the local atmospheric environment.

The most abundant species (concentrations generally higher than 1 µg m⁻³) in PM₁₀ are OC, SO₄²⁻, NO₃⁻, Cl⁻, BC, Na⁺, Ca and NH₄⁺. OC, SO₄²⁻, NO₃⁻, BC, and NH₄⁺ are the largest components of PM_{2.5}, while Cl⁻, Na⁺ and Ca are abundant mainly in the coarse particle fraction. This fact is consistent with expected contribution from anthropogenic sources for PM_{2.5} and from marine aerosol and suspended dust for PM_{10-2.5}. Mainly in the summer, NO₃⁻ is also found abundantly in the coarse particle fraction, presumably because of photochemically produced gaseous nitric acid reaction with marine and mineral coarse particles and the existence of higher temperatures that hinder the competitive formation of ammonium nitrate fine particles (Rodríguez et al., 2002).

Due to the geographical position, ocean contribution is significant in every sample, irrespective of air mass characteristics. Thus, sea spray ion concentrations (Na⁺, Cl⁻, Mg²⁺) are higher in Portuguese coastal areas than in more continental European regions (Putaud et al., 2004). Samples with Maritime trajectories are particularly rich in these ions, which are present mainly in the coarse fraction. Therefore, the total mass ratio fine/coarse fractions, for these air masses, is the lowest.

The predominant anthropogenic species (SO₄²⁻, NH₄⁺, NO₃⁻, OC and BC) show concentrations in the same range of values observed in other European urban/industrial areas (or even lower) (Putaud et al., 2004). Analysis of the results, according to air mass characteristics, shows that maritime samples present the lowest concentrations, for compounds emitted by anthropogenic sources. This fact could be attributed to the transport of cleaner air masses from the sea and to the existence of better vertical dispersion conditions during these events.

Mineral elements (Al, Si, Ca, Sc, Fe, La and Sm) reached the highest concentrations during South Continental air mass transport. This is due to an important contribution of long range transported soil emissions, namely from the interior of Iberian Peninsula and the Saharan desert (Almeida, 2004). On 11 October 2001, a Sahara transport event resulted in concentration peaks for Al, Si, Ca and Fe of 2630, 7860, 6450, and 4080 ng m⁻³, respectively. Therefore, air mass transport from Africa is usually associated with very high PM concentrations (Rodríguez et al., 2001).

On average, the total aerosol mass concentration varies little throughout the year. The temporal patterns can be explained by weather and human activities. During spring and summer there is a greater contribu-

tion of SO₄²⁻ and soil derived constituents that reflects in higher levels of Al, Si, Ca, Cs, La and Sm, while in the autumn and winter there is a more important loading of sea spray and anthropogenic derived particulate compounds, as result of lower mixing heights, that inhibit the dispersion of pollutants.

4. Source apportionment

The fine/coarse ratio has commonly been used as a first step in attempting to identify natural and anthropogenic sources of particles. In Table 1, the fine/coarse average shows that, for V, Ni, As, Se, Br, Sb, Hg, Pb, SO₄²⁻, NO₃⁻, NH₄⁺, K⁺, OC and BC, the fine fraction clearly has higher contents than the coarse fraction, indicating the probable provenience of these compounds from anthropogenic activities. For Al, Si, Ca, Sc, Ti, Mn, Fe, La, Sm, Cl⁻, Na⁺ and Mg²⁺, the coarse fraction is more important than the fine fraction. Cl⁻, Na⁺ and Mg²⁺ probably emanate from the ocean, whereas Al, Si, Ca, Sc, Ti, Mn, Fe, La and Sm reflect a soil contribution.

The crustal enrichment factor method has been used as an attempt to evaluate the strength of the crustal and non-crustal origin. Enrichment factors, using Sc as a crustal reference element (EF_{Sc}) were calculated based on Eq. (1) and using Mason and Moore (1982) soil composition (Fig. 2):

$$EF_{Sc} = \frac{([X]/[Sc])_{PM}}{([X]/[Sc])_{crust}} \quad (1)$$

EF_{Sc} higher than 10 can be observed for V, Ni, Cu, Zn, As, Se, Br, Sb and Pb, suggesting strong anthropogenic contribution. In the coarse fraction, these elements present lower EF_{Sc}, being probably associated with a resuspension origin from ground.

PCA applied to the fine and coarse particulate compounds identified seven main chemical profiles

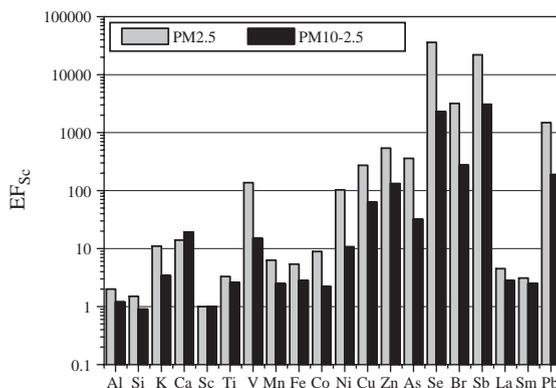


Fig. 2. Enrichment factor using Sc as a reference element and Mason and Moore (1982) soil composition.

Table 2
VARIMAX normalized rotated factor loading and communalities obtained in PCA applied to the aerosol fine fractions

PM _{2.5}	PC1 Soil	PC2 Fuel comb.	PC3 Sea	PC4 Se/Hg	PC5 Second	PC6 Ind./traffic	PC7 Vehicle exh.	Comun.
Al	0.95							0.96
Si	0.97							0.98
Sc	0.98							0.99
Ti	0.91							0.88
V		0.92						0.94
Mn	0.80					0.28		0.82
Fe	0.90					0.23		0.97
Co	0.52	0.64					0.30	0.82
Ni		0.90			0.20			0.94
Cu			0.22			0.77	0.30	0.79
Zn						0.66		0.63
As		0.38				0.40	0.70	0.82
Se				-0.99				0.97
Br		0.28	-0.41				0.25	0.48
Sb			0.26			0.68		0.50
La	0.96							0.98
Sm	0.98							0.99
Hg				-0.99				0.97
Pb		0.60				0.45	0.21	0.68
Cl ⁻			-0.78		-0.48			0.84
NO ₃ ⁻		0.22					0.81	0.84
SO ₄ ²⁻					0.96			0.97
K ⁺	0.20				0.28		0.73	0.59
Na ⁺			-0.88				-0.32	0.97
Ca ²⁺	0.60	0.27			0.32			0.64
Mg ²⁺			-0.88				-0.29	0.97
NH ₄ ⁺					0.83		0.41	0.97
Eigenvalues	7.8	3.0	2.6	2.1	2.2	2.2	2.4	22.3
% total var. expl.	29.0	11.1	9.7	7.6	8.2	8.0	9.0	82.6

Only factor loadings with absolute values greater than 0.2 are presented and factor loadings with absolute values greater than 0.65 are presented in bold. Eigenvalues obtained for each of the factors and percentage of variance explained for each factor.

sources contributing to PM_{2.5} (Table 2): soil, fuel oil combustion, sea spray, a Se/Hg emission, secondary aerosol, coal combustion and traffic. These sources account for 83% of the total variance in the PCA. For PM_{10-2.5}, PCA identified six sources, which account for 88% of the total variance: soil, sea spray, fuel oil combustion, secondary aerosol, coal combustion/traffic, and a Se/Hg emission source (Table 3).

4.1. Mineral aerosol

In both fractions, the first principal component (PC) represents crustal contribution, given that it presents high factor loadings for Al, Si, Sc, Ti, Mn, Fe, La, Sm and Ca²⁺, which are typical soil elements and have a similar seasonal evolution.

In the coarse particles fraction, EF_{Sc} reveal the existence of one major common source contributing for all these elements, which is probably the crust. In

PM_{2.5}, the EF_{Sc} are higher, especially for Ca, Mn, Fe and La. However, the local crustal composition was not determined experimentally and, therefore, this enrichment may be unreal. Therefore, the local soil X/Sc ratio was inferred by calculating the slope of the linear regression applied to the coarse fraction X/Sc data, considering, by approximation, that in this size range crust is the only source for these elements.

Significant enrichments were identified for fine Al, Si, Ca, Ti, Mn and Fe concentrations. The excess in relation to the crustal composition was calculated based on Eq. (2) (where (X/Sc)_{crust} was inferred from the coarse fraction results) and introduced in a PCA (table not shown)

$$[X]_{\text{excess}} = [X]_{\text{PM}} - [\text{Sc}]_{\text{PM}} \left(\frac{X}{\text{Sc}} \right)_{\text{crust}} \quad (2)$$

PCA results reveal an association between the Fe_{excess} and vehicle emission (factor loading α equal to 0.43) and

Table 3
VARIMAX normalized rotated factor loading and communalities obtained in PCA applied to the aerosol coarse fractions

PM _{10-2.5}	PC1 Soil	PC2 Sea	PC3 Fuel comb.	PC4 Second.	PC5 Se/Hg	PC6 Ind./traffic	Comun.
Al	0.89					0.25	0.98
Si	0.94		0.21				0.99
Sc	0.98						1.00
Ti	0.97						0.98
V	0.35		0.86			0.20	0.96
Mn	0.92		0.24				0.98
Fe	0.92		0.26			0.22	1.00
Co	0.78		0.52				0.96
Ni	0.44		0.80			0.25	0.97
Cu	0.50	0.34	0.35			0.51	0.92
Zn	0.24					0.86	0.78
As	0.42		0.78			0.34	0.96
Se					-0.93		0.78
Br		-0.35	0.81				0.83
Sb	0.38	0.28	0.46			0.59	0.91
La	0.96						1.00
Sm	0.98						1.00
Hg					-0.94		0.80
Pb	0.23		0.36			0.76	0.86
Cl ⁻		-0.94					0.98
NO ₃ ⁻	0.23			0.78			0.87
SO ₄ ²⁻		-0.69		0.56			0.86
K ⁺		-0.94					0.95
Na ⁺		-0.92				-0.21	0.94
Ca ²⁺	0.57			0.59		0.42	0.91
Mg ²⁺		-0.93				-0.21	0.93
NH ₄ ⁺				0.86			0.70
K—non-soluble	0.87			0.28			0.95
Ca—non-soluble	0.65					0.43	0.87
Eigenvalues	10.4	4.4	3.8	2.3	1.9	2.9	25.7
% total var. expl.	36.0	15.2	13.0	7.8	6.5	10.0	88.2

Only factor loadings with absolute values greater than 0.2 are presented and factor loadings with absolute values greater than 0.65 are presented in bold. Eigenvalues obtained for each of the factors and percentage of variance explained for each factor.

industry/traffic ($\alpha = 0.49$). Mn_{excess} presents a high factor loading ($\alpha = 0.69$) for industry/traffic. Al_{excess} and Si_{excess} are associated with secondary aerosol, showing their probable association with fly ash from industrial, or energy production, combustion processes. Ti_{excess} presents an association with Hg and Se emission and with fuel oil combustion. Ca_{excess} shows a strong anticorrelation ($\alpha = -0.92$) with the mineral aerosol.

In Bobadela, the influence of African dust inputs is evident in the time series of crustal components in PM. Levels of Al, Si, Sc, Ti, Mn, Fe, La and Sm reached the highest concentrations during African dust events (Almeida, 2004). In the south of Europe and specifically in the Iberian Peninsula soil dryness and the poor soil coverage by vegetation, associated with suitable meteorological conditions, (high convective atmospheric dynamics) favour re-suspension processes (Artiñano et al., 2001).

Moreover, Sahara desert is responsible for the global emission of 50% of the total mass of mineral aerosols to the atmosphere (Pacyna, 1998). Therefore, South Continental-originated samples are characterized by the simultaneous increase of PM and mineral aerosol levels.

The various analytical methodologies employed allowed the determination of the soluble and total fractions of several elements and, by difference, the concentration of the insoluble constituents. In the coarse fraction, important levels of insoluble K and Ca were determined, especially with samples from non-maritime air masses. Therefore, in PM_{10-2.5}, PCA was performed with the soluble and insoluble forms of these two elements. PCA reveals that while soluble potassium is associated mainly with sea spray; insoluble potassium is associated mainly with aluminium and silicon in the mineral aerosol PC.

4.1.1. Marine aerosol

PC3, in the fine fraction, and PC2, in the coarse fraction, correlate with Na^+ , Cl^- and Mg^{2+} and represent marine aerosol emissions. In the coarse fraction, SO_4^{2-} and K^+ also correlate well with this component.

Fig. 3 shows the relation between Cl^- and Na^+ for (a) $\text{PM}_{2.5}$ and (b) $\text{PM}_{10-2.5}$. The line represents bulk sea water weight concentration ratio ($\text{Cl}^-/\text{Na}^+ = 1.8$) (Bowen, 1979). In the coarse fraction, it is evident that chloride is strongly associated with sodium. The slope of the regression line (1.5) compares quite well with $[\text{Cl}^-]/[\text{Na}^+]$ ratio for bulk sea-water, revealing a common origin in the sea. In the fine fraction, the pattern of values suggests an unstable relation between these elements. Nearly all points are located below the bulk sea-water ratio line. The deficit has been suggested to be the result of the reaction of NaCl with acidic species (HNO_3 , SO_2 and H_2SO_4) leading to a displacement of Cl^- as HCl (Pio and Lopes, 1998). The enrichment of Cl^- for some samples is probably due to the emission of Cl^- by industrial sources and motor vehicles, with/or formation of NH_4Cl from gaseous precursors (Almeida, 2004).

The average chloride loss is 50% for $\text{PM}_{2.5}$ and 26% for coarse particles. The percentage of chloride lost from sea-salt particles decreases with increasing particle size because smaller particles have higher surface-to-volume ratio and longer atmospheric residence time (Harrison and Pio, 1983).

Due to the semi-permanent Azores high-pressure and the Icelandic low-pressure systems over North Atlantic Ocean, Portugal is characterized by a dominant westerly wind regime. Therefore, PM levels were found to be highly affected by significant amounts of oceanic emissions, transported by this prevailing wind regime (Almeida, 2004).

4.1.2. Fuel oil combustion

In PC2, in the fine fraction, and PC3, in the coarse fraction, the association between V and Ni strongly suggests fuel oil combustion processes. The fuel oil

power plant located in this industrial area is probably an important contributor to V and Ni particulate levels observed at the sampling site.

Normally these elements are present mostly in fine fraction; however, in this region, the levels of Ni and V are of the same order of magnitude in coarse and fine particles. Regarding the EF_{Sc} results, probably, fine V and Ni provide directly from industrial combustion, whereas coarse fraction V and Ni result also from resuspension of dust.

4.1.3. Secondary aerosol

SO_4^{2-} and NH_4^+ —which derive from gas to particle conversion processes from SO_2 oxidation and NH_3 neutralization—are the main compounds defining the fifth PC in the fine fraction. These ions present a strong association, mainly in summer, which indicates that SO_4^{2-} is mostly present as ammonium sulphate (Fig. 4). In winter, ammonium is in excess, in relation to sulphate, and is therefore also associated with other anions (mainly nitrates). This maybe due to the stronger solar radiation in summer, increasing both temperature and the formation of OH radicals, promoting therefore the formation of secondary sulphates which are transported at longer distances than the gaseous precursors (Chan et al., 1999).

In the coarse fraction, PC4 represents the secondary aerosol production. This PC also presents important factor loadings for NO_3^- , NH_4^+ and Ca^{2+} . Ammonium nitrate distributes usually into larger size ranges than ammonium sulphate because of its capability to multi-evaporation-condensation steps (Harrison and Pio, 1983). In this size range, NO_3^- is also attributed to the reaction of gaseous HNO_3^- (produced from oxidation of NO_2 or from re-evaporation of sub-micron NH_4NO_3 particles) with mineral species such as calcium carbonate and with sea-salt to form $\text{Ca}(\text{NO}_3)_2$ and NaNO_3 , respectively. These reactions are predominant in the warm season, whereas in the winter NO_3^- reacts with NH_3 to form NH_4NO_3 .

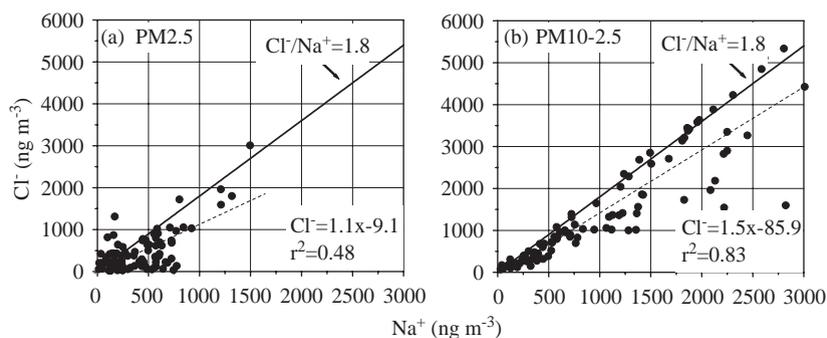


Fig. 3. Relation between Cl^- and Na^+ for (a) fine and (b) coarse fractions (Cl^-/Na^+ ratio for sea water (Bowen, 1979), (—) linear regression for fine and coarse fractions).

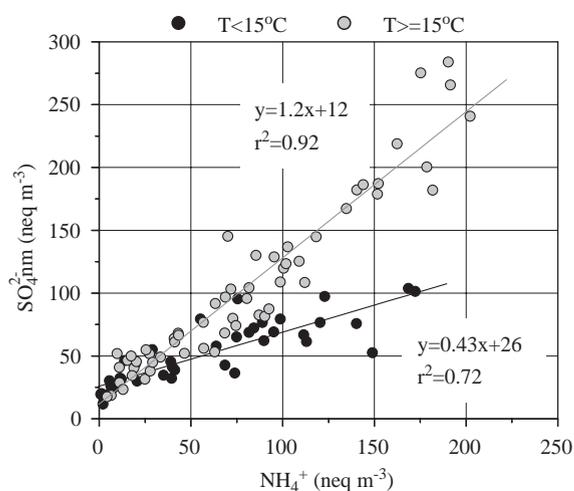


Fig. 4. Relation between SO_4^{2-} and NH_4^+ concentrations (neq m^{-3}) for temperatures lower and higher than 15°C .

4.1.4. Vehicle exhausts

In the fine fraction, nitrates, in spite of having usually also a secondary origin, do not integrate the secondary aerosol PC, due probably to the influence of different sources and different formation processes. These processes are highly affected by meteorological conditions, which promote higher SO_4^{2-} concentrations in summer and higher NO_3^- concentrations in winter. Seasonal evolution of nitrate is induced by the higher thermal stability of particulate ammonium nitrate compounds in cold seasons.

NO_3^- presents a strong correlation with PC7 that represents almost exclusively road vehicle exhaust emissions (Weckwerth, 2001; Samara et al., 2003; Pio et al., 1996). The reaction of NO_x to form nitric acid is quite rapid regardless of meteorological conditions (Harrison et al., 1997) therefore, the particulate nitrate associates preferably with the PC representing local sources of precursor pollutants. Similar behaviour was observed previously in Portuguese rural/coastal areas (Pio et al., 1996). In a further attempt to confirm the association of this component with vehicle exhaust, PCA was performed with $\text{PM}_{2.5}$ constituents, adding two important vehicle emission tracers—organic and black carbon (despite the fact that only 61 samples could be analysed for these two components). PCA results (table not shown) revealed a strong correlation between organic and black carbon and this PC, confirming an association between this component and the vehicle exhaust.

4.1.5. Industry/traffic

Zn, Cu, Sb and Pb are correlated with PC6 in the fine and coarse fractions. These elements are usually associated with various different sources nominally coal

combustion, incineration and traffic (mainly tires and brake wear, rather than combustion processes) (Sternbeck et al., 2002).

A PCA was performed with the $\text{PM}_{10-2.5}$ constituents adding the organic and black carbon, in a further attempt to confirm the association of this component with traffic (table not shown). PCA presented a strong correlation between organic and black carbon and this PC confirming an association between this component and the traffic.

4.1.6. Se/Hg emission

Hg and Se present a high correlation with PC4, in the fine fraction, and PC5, in the coarse fraction. The emission of these elements is probably local, because the main maximums in fine and coarse fractions are common. At the end of year 2001, the sudden increase of Hg and Se concentrations (50 times for Hg and 400 times for Se) was associated with winds providing from the industrial area located North of Lisbon, confirming the probable local origin of these species with origin on an unidentified industrial process (Almeida, 2004; Freitas et al., 2005).

4.2. Source contribution

Results for each sample and for seasonal averages of the MLRA applied to the modified PC scores are given in Figs. 5 and 6. MLRA shows that in average, the largest contribution to $\text{PM}_{2.5}$ total mass is the secondary aerosol (25%) and vehicle exhaust (22%). Mineral aerosol from soil contributes with 16%, industry/traffic with 14%, Fuel oil combustion with 8%, marine aerosol with 8% and Se/Hg emission with 0.2%. Source contribution presents seasonality, characterized by higher contributions of secondary aerosol (34%), during spring/summer, due to the photochemical reactions; and higher vehicle exhaust (30%) contributions during autumn/winter, associated with the preferential formation of ammonium nitrate at lower winter temperatures.

In the coarse fraction, marine (47%) and soil (20%) contributions are predominant (Fig. 6). Secondary aerosol contribution decreases to 15% in these coarse particles. Fuel oil combustion, industry/traffic and Se/Hg emissions have an average contribution of 5%, 13% and 0.4%, respectively. Sea spray presents a higher aerosol load in the first half of the year, due to the more frequent influence of maritime air masses transport to the site during this period. In the coarse fraction, soil contribution is higher in spring/summer, probably due to the re-suspension of mineral particles, which is facilitated by and higher desegregation of the particles in dryer months.

The average source contributions were calculated for the main types of air masses trajectories (Fig. 7). The lowest total source contribution was registered in

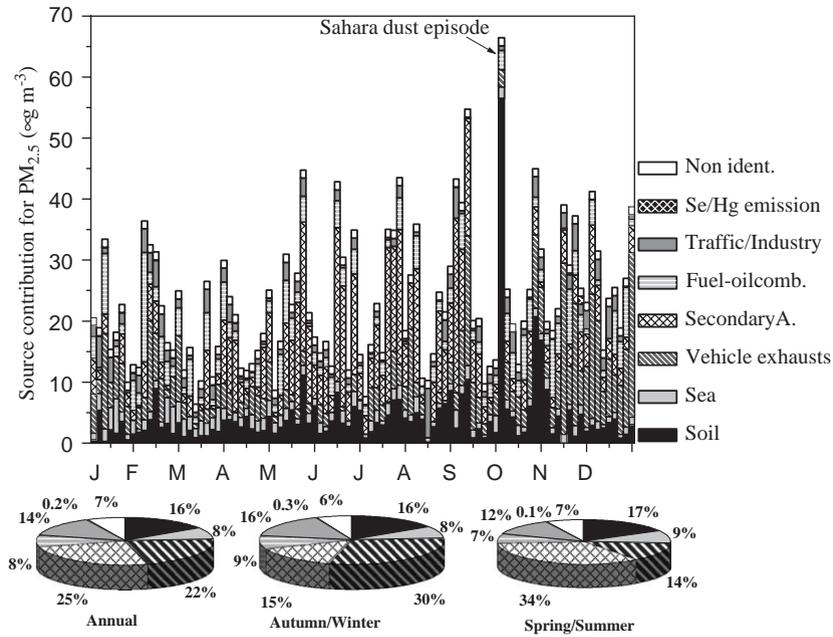


Fig. 5. Source contribution for $PM_{2.5}$ total mass concentration time series ($\mu\text{g m}^{-3}$). Average relative source contribution to $PM_{2.5}$ mass concentration during all the year, autumn/winter and spring/summer.

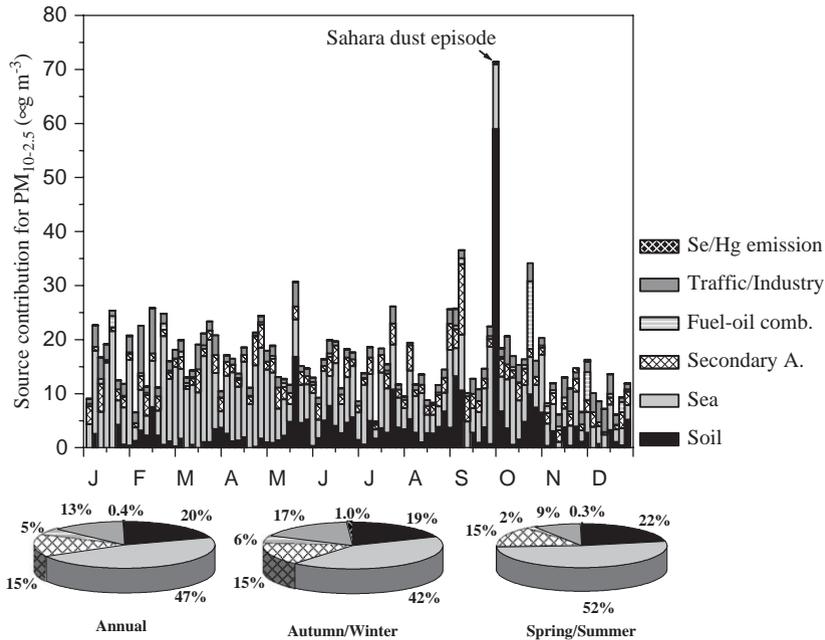


Fig. 6. Source contribution for $PM_{10-2.5}$ total mass concentration time series ($\mu\text{g m}^{-3}$). Average relative source contribution to $PM_{10-2.5}$ mass concentration during all the year, autumn/winter and spring/summer.

samples associated with maritime air mass trajectories. In these samples, $PM_{2.5}$ and $PM_{10-2.5}$ levels reached 15 and $16 \mu\text{g m}^{-3}$, respectively. These scenarios are usually associated with the transport of cleaner air masses from

the Atlantic Ocean and with better dispersion conditions of pollutants providing from the industrial area. These conditions promote a lower contribution from anthropogenic and mineral sources and a higher contribution

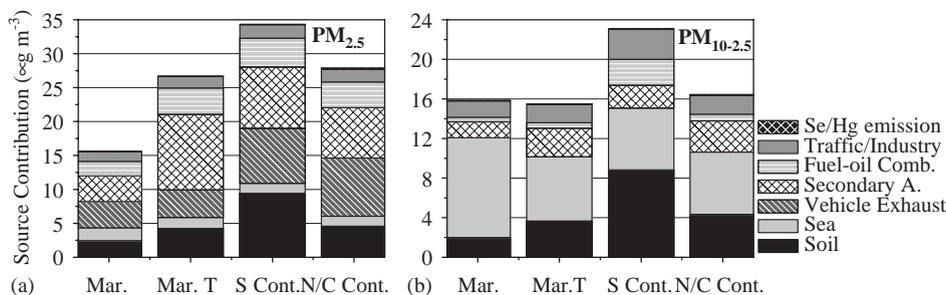


Fig. 7. Source contribution to (a) $PM_{2.5}$ and (b) $PM_{10-2.5}$ concentrations ($\mu\text{g m}^{-3}$), discriminated by air mass type (Mar.—maritime air masses, Mar. T—maritime transformed air masses, S Cont.—South Continental air masses, N/C Cont.—North/centre Continental air masses).

from the sea. For maritime samples the average contribution of anthropogenic sources was 11 and $3.8 \mu\text{g m}^{-3}$, which accounts for 72% of $PM_{2.5}$ total mass and 24% of $PM_{10-2.5}$ total mass, respectively. The sea contribution for this trajectory is, on average, 19 and $10 \mu\text{g m}^{-3}$, which accounts for 12% of $PM_{2.5}$ total mass and 64% of $PM_{10-2.5}$ total mass, respectively.

The highest mineral dust loads in $PM_{2.5}$ and $PM_{10-2.5}$ were recorded in South Continental air mass trajectories, indicating a strong contribution of long-range transport for the mineral aerosol. For these samples mineral component contributes, on average, with 9.4 and $8.8 \mu\text{g m}^{-3}$, which accounts for 27% of $PM_{2.5}$ total mass and 38% of $PM_{10-2.5}$ total mass, respectively.

5. Conclusion

Composition of $PM_{2.5}$ and $PM_{10-2.5}$ was investigated in order to identify the main sources affecting an industrial/urban area with a special geographical position—20 km northeast of the southwest European coast.

Source apportionment results show that the major $PM_{2.5}$ aerosol mass contributors include secondary aerosol (25%) and vehicle exhaust (22%). In the coarse fraction, marine (47%) and mineral (20%) aerosol contributions are predominant.

Natural sources significantly affect $PM_{10-2.5}$ levels, whereas anthropogenic sources affect mainly the fine fraction. Nowadays in this region, road transport and secondary aerosol formation dominate over specific industrial emissions, even in the presence of large and numerous industrial sources.

The highest $PM_{10-2.5}$ levels were recorded during South Continental episodes. These episodes are characterized by high mineral aerosol contents, due to the transport of dust from the interior of Iberian Peninsula and the Sahara desert. Maritime air mass transport has a significant role on particulate air quality in the North of Lisbon. Maritime transport scenarios are very frequent and promote the decrease of anthropogenic and mineral

aerosol concentrations. Therefore, measurement of $PM_{2.5}$ is a better methodology to access the impact of anthropogenic activities on air quality, than PM_{10} , in coastal south European urban areas. PM_{10} is highly influenced by coarse particles ($2.5 \mu\text{m} < DA < 10 \mu\text{m}$) of natural origin in the ocean (sea spray) and land surface (wind blown dust). $PM_{2.5}$ still contains important contributions from sea spray and dust natural emissions (of the order of 25%) but its main source contributions are from anthropogenic activities associated with thermal energy production and road traffic.

After identifying the contribution of PM sources, it is possible to conclude that the abatement strategies to improve air quality should focus on traffic and on non-mobile combustion processes emitting sulphur and NO_x , which conduce to the formation of secondary aerosols.

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