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Impact of Maritime Air Mass Trajectories on the Western European Coast Urban Aerosol

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IMPACT OF MARITIME AIR MASS TRAJECTORIES ON THE WESTERN EUROPEAN COAST URBAN AEROSOL

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Lisbon is the largest urban area in the Western European coast. Due to this geographical position the Atlantic Ocean serves as an important source of particles and plays an important role in many atmospheric processes. The main objectives of this study were to (1) perform a chemical characterization of particulate matter ($PM_{2.5}$) sampled in Lisbon, (2) identify the main sources of particles, (3) determine PM contribution to this urban area, and (4) assess the impact of maritime air mass trajectories on concentration and composition of respirable PM sampled in Lisbon. During 2007, $PM_{2.5}$ was collected on a daily basis in the center of Lisbon with a Partisol sampler. The exposed Teflon filters were measured by gravimetry and cut into two parts: one for analysis by instrumental neutron activation analysis (INAA) and the other by ion chromatography (IC). Principal component analysis (PCA) and multilinear regression analysis (MLRA) were used to identify possible sources of $PM_{2.5}$ and determine mass contribution. Five main groups of sources were identified: secondary aerosols, traffic, calcium, soil, and sea. Four-day backtracking trajectories ending in Lisbon at the starting sampling time were calculated using the HYSPLIT model. Results showed that maritime transport scenarios were frequent. These episodes were characterized by a significant decrease of anthropogenic aerosol concentrations and exerted a significant role on air quality in this urban area.

The Clean Air for Europe program estimated that approximately 350,000 premature deaths occur annually due to exposure to ambient air fine particulate matter ($PM_{2.5}$) (Amann et al., 2005). Adverse effects attributed to air pollution by $PM_{2.5}$ are especially important where dense urban populations are exposed to anthropogenic emissions. These observations convinced policymakers to legislate more and more stringent emission and air pollution limit levels. Therefore, in urban areas the identification of pollutant sources and a reliable estimation of their contribution to $PM_{2.5}$ levels are essential to develop efficient markers of transport to initiate actions for mitigation to achieve legislated levels and reduce adverse health effects.

In urban areas traffic emissions are the predominant source of PM not only due to vehicle exhaust but also due to resuspension of particles from the road surface (Almeida et al., 2006a). In addition to the local and regional PM sources, the levels and physical and chemical properties of ambient air PM (Ghio et al., 2012) depend also on climatology mainly temperature, humidity, photochemistry, resuspension of soil particles, rain scavenging potential, recirculation of air masses, and stability, as well as on geography, including proximity to the coast, topography, soil cover, and proximity to arid zones of a given region (Pérez et al., 2008). Therefore, wide variations in PM levels and characteristics may be expected when considering different European locations (Putaud et al., 2010).

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Due to the geographical position of Lisbon on the extreme southwest of Europe and to the dominant western wind regime, this nation is influenced by the presence of the semipermanent Azores high-pressure and the Icelandic low-pressure systems over the North Atlantic Ocean; thus, maritime effects are important for this urban aerosol. The main objectives of this study were to (1) perform a chemical characterization of $PM_{2.5}$ sampled in Lisbon; (2) identify sources of PM; (3) quantify their contributions to $PM_{2.5}$; and (4) assess the impact of the geographical localization of Lisbon with respect to concentration and composition of respirable particles.

EXPERIMENTAL

Site Description

$PM_{2.5}$ was sampled in Lisbon during the year 2007. Lisbon is the capital and largest city of Portugal, with a population of 564,657 within its administrative boundaries on a land area of 84.8 km^2. The urban area of Lisbon extends beyond the administrative city limits with a population of 2.4 million on an area of 958 km^2. Lisbon is the westernmost large city located in Europe, as well as its westernmost capital city and the only one along the Atlantic coast. The sampling station was located in the urban center of Lisbon (Av. Rovisco Pais, 38°44′N; –9°8′W), 4 km from the Tagus Estuary valley and 20 km from the Atlantic Ocean (Figure 1), and surrounded by high-density traffic roads.

APM Sampling and Analysis

$PM_{2.5}$ was collected for 24-h periods (starting at 0:00 and ending at 23:59) during 365 d. Sampling was conducted with a Partisol sampler operating at a flow rate of 16 L/min. Aerosol samples were collected on Teflon filters with 47 mm diameter. The filter loads were measured by gravimetry. Filter weight before and after sampling was obtained as the mean of three measurements. The exposed filters were cut into two parts: One was analyzed by k_0-based instrumental neutron activation analysis (k_0-INAA) (Bowen and Gibbons, 1963; De Corte, 1987) for elemental characterization and the other was analyzed by ion chromatography (IC) (Chow and Watson, 1999) for water-soluble ion determination.

For elemental analysis, filters halves were rolled up, placed into a polyethylene container and irradiated for 5 h at a thermal neutron flux of 1.03×10^{13} cm^{-2} s^{-1} in a Portuguese Research Reactor. For each irradiated sample two gamma spectra were measured with hyperpure germanium detectors: one spectrum 2–3 days after the irradiation and the other one after 4 wk. The k_0-INAA method was used and 0.1% Au–Al discs were co-irradiated as comparators. The concentrations of the elements Na, K, Sc, Fe, Co, Zn, As, Se, Br, Sb, and La were determined in $PM_{2.5}$ filters. Tests of reproducibility within filters and between filters were conducted using parallel sampling with two similar sampling units and measuring the particle species by k_0-INAA. Results were reproducible to within 5–15%, providing reliable support for the validity of the analytical techniques (Almeida et al., 2003a, 2003b). The accuracy of analytical methods was evaluated with NIST filter standards, revealing results with an agreement of ±10% (Almeida et al., 2006b).

For water-soluble ions determination, filter halves were extracted with distilled deionized water by ultrasonic and mechanical shaking and filtered through a prewashed Whatman 42 filter. The aqueous extract was analyzed by IC to determine concentrations of Cl^-, NO_3^-, SO_4^{2-}, Ca^{2+}, Mg^{2+}, Na^+, and K^+. Further, for quality assurance during the sampling campaign, 15 blank filters were treated the same way as regular samples. All measured species were homogeneously distributed; therefore, concentrations were corrected by subtracting the filter blank contents.

Air Quality Monitoring Network

This study also used $PM_{2.5}$ measurements performed in two Lisbon monitoring stations: Entrecampos classified as an urban traffic station and Olivais considered as an urban background station. These stations belong to the Portuguese Environment Agency (APA) Air Quality Monitoring Network. Beta-attenuation monitors were used for $PM_{2.5}$ automatic measurements.

Air Mass Trajectories, PCA and MLRA Procedures

For each starting sample date, 4-d backtracking trajectories ending in Lisbon were calculated using the HYSPLIT model (Draxler, 2009) at 50, 500, and 1000 m height and the vertical velocity option. According to the backtracking trajectories, air masses arriving in Lisbon during the sampling campaign were classified into three main groups: (1) Sea: Maritime air masses, if backtracking trajectories indicated an ocean origin without continental contamination during the previous 4 d; (2) S Cont.: South Continental air masses, if backtracking trajectories indicated an African or Southern Europe origin; and (3) NC Cont.: North/Center Continental air masses, if backtracking trajectories indicated an origin in the North or Central Europe. Samples associated with ocean origin trajectories, with a final recirculation through the Iberian Peninsula,or trajectories that indicated an European origin with a final recirculation through the ocean were considered as “other” in Figure 1.

Sources categories for $PM_{2.5}$ constituents were identified by means of principal component factor analysis (PCA) using STATISTICA software according to the methodology described by Almeida et al. (2005). This was performed by utilizing the orthogonal transformation method with Varimax rotation and retention of principal components whose eigenvalues were greater than unity. Factor loadings indicated 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 were retained for PCA analysis. The contribution of each source group to the aerosol burden was then quantitatively assessed by means of a multilinear regression analysis (MLRA). MLRA was applied to the experimental data, using as dependent variables $PM_{2.5}$ total mass concentrations and as independent variables the species that had the highest factor loading in each factor. The result of this analysis was the daily contribution of the different sources to $PM_{2.5}$ levels, which then enabled interpretation of seasonal patterns of source contributions. The nonparametric Mann–Whitney *U*-test was used to compare the contribution of sources for each air mass trajectory type. Statistical significance was set as $p < 0.05$. Statistical calculations were performed using STATISTICA software.

RESULTS AND DISCUSSION

$PM_{2.5}$ Concentrations

Figure 1 shows the frequency of the air masses trajectories that affected Lisbon during the year 2007. It is clear that Lisbon aerosol was markedly affected by maritime aerosol, either by pure sea trajectories (37%) or by ocean-origin trajectories with a final recirculation through the Iberian Peninsula. The trajectories indicated a European origin with a final recirculation through the ocean (39%). In order to assess the influence of different air mass trajectories for the aerosol, Table 1 presents mean concentrations and respective standard deviation for $PM_{2.5}$ constituents not only for all samples but also for those differentiated by air mass trajectories type. In 2007, the mean concentration measured in the center of Lisbon was 18 $\mu g/m^3$. Compared with other European urban areas, mass concentrations were in general lower than levels measured in Southern and Central Europe and in the same range of values of Northwestern Europe (Putaud et al., 2010). Table 1 shows that samples associated with air mass trajectories coming from the sea presented significantly lower $PM_{2.5}$ concentrations compared with samples associated with South Continental and North/Center Continental air masses.

The European Directive 2008/50/EC of 21 May 2008 on ambient air quality and cleaner air for Europe established two stages for $PM_{2.5}$ annual limit value concentrations.

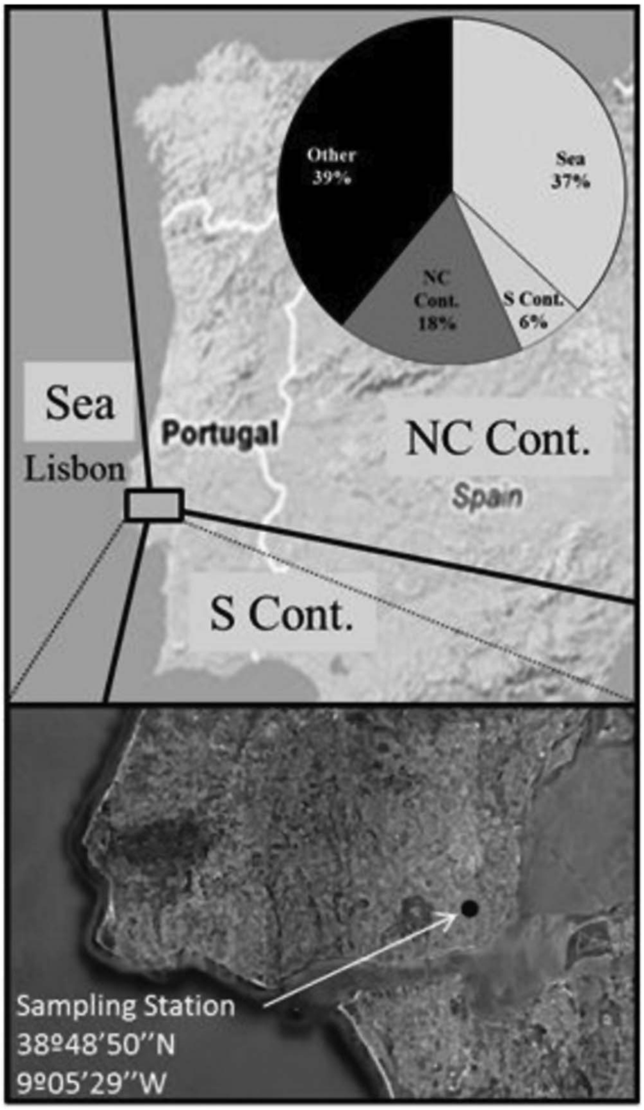

FIGURE 1. Sampling localization and air mass trajectories sectors categorization and frequency (Sea, maritime air masses; S. Cont, South Continental air masses; N/C Cont, North Center Continental air masses).

Stage 1 indicates that the annual limit value for this pollutant is 25 $\mu g/m^3$ and that the date by which the limit value is to be attained is 1 January 2015. In Stage 2, the annual limit value is set at 20 $\mu g/m^3$ and is to be attained by 1 January 2020. The directive itself states that these indicative limit values must be reviewed by the commission in 2013 in light of further information on health and environmental effects, technical feasibility and experience of the target value (25 $\mu g/m^3$ on January 1, 2010) (EU, 2008). Both target values were not exceeded in the sampling campaign performed in 2007.

The U.S. Environmental Protection Agency (EPA) set the permitted annual maximum concentration at 15 $\mu g/m^3$ (U.S. EPA, 2006). The World Health Organization (WHO) established an annual average concentration of 10 $\mu g/m^3$ as the long-term guideline values for $PM_{2.5}$ (WHO, 2006). This value represents the lowest value at which total, cardiopulmonary, and lung cancer mortality were found to increase with more than 95% confidence in response

TABLE 1. Mean concentrations of elements and water soluble ions measured in $PM_{2.5}$ (values in ng/m^3) for all samples and discriminated by air mass trajectories (Sea, maritime; S. Cont., South Continental; NC Cont., North/Center Continental)

	All ($n = 348$)	Sea ($n = 128$)	CS ($n = 22$)	CNC ($n = 61$)
$PM_{2.5}$	$18,000 \pm 12,000$	$13,000 \pm 7700$	$22,000 \pm 13,000$	$23,000 \pm 15,000$
SO_4^{2-}	2800 ± 2200	1800 ± 1400	2900 ± 2200	3300 ± 2000
NO_3^-	1600 ± 2800	910 ± 1100	2000 ± 2700	2600 ± 4400
NH_4^+	1300 ± 1100	760 ± 800	1300 ± 990	1700 ± 1100
Na^+	390 ± 320	540 ± 380	310 ± 270	240 ± 190
Cl^-	290 ± 340	400 ± 400	300 ± 270	220 ± 270
K	220 ± 190	140 ± 140	340 ± 260	300 ± 170
K^+	160 ± 140	100 ± 95	220 ± 180	150 ± 160
Ca^{2+}	160 ± 73	140 ± 65	200 ± 100	190 ± 80
Fe	160 ± 180	140 ± 250	240 ± 250	160 ± 85
Mg^{2+}	46 ± 39	64 ± 44	40 ± 33	27 ± 21
Zn	32 ± 28	21 ± 22	38 ± 31	45 ± 30
Br	4.9 ± 9.8	5.7 ± 15	3.1 ± 2.8	4.6 ± 3.5
Sb	1.8 ± 2.0	1.4 ± 2.1	2.3 ± 2.0	2.7 ± 2.6
Se	0.73 ± 0.63	0.63 ± 0.80	0.69 ± 0.43	0.76 ± 0.43
As	0.61 ± 0.86	0.42 ± 0.83	1.2 ± 1.6	0.72 ± 0.59
Co	0.16 ± 0.23	0.15 ± 0.19	0.16 ± 0.12	0.16 ± 0.11
La	0.13 ± 0.20	0.11 ± 0.28	0.19 ± 0.22	0.13 ± 0.084
Sc	0.032 ± 0.099	0.064 ± 0.18	0.043 ± 0.081	0.014 ± 0.014

to long-term exposure to $PM_{2.5}$ (Samet and Krewski, 2007; Cohen et al 2005; Krewski et al, 2004; Pope et al., 2002). In 2007, both $PM_{2.5}$ U.S. EPA limit value and WHO guideline were exceeded.

Figure 2 shows the $PM_{2.5}$ annual average concentrations measured by the Portuguese Environment Agency (APA) Air Quality Monitoring Network since 2003 to 2008. Besides the significant decrease of $PM_{2.5}$ concentrations since 2003, in order to achieve the ambitious goal proposed by WHO and to reduce the levels of $PM_{2.5}$, the country needs to adopt an increasingly more stringent set of standards and track progress through monitoring of emission reductions.

The major species that had concentrations generally higher than 1 μg/m^3 measured in $PM_{2.5}$ were SO_4^{-2}, NO_3^-, and NH_4^+. These species are principally associated with anthropogenic sources and secondary production mechanisms. Samples associated with air mass trajectories originating from the sea presented significantly lower SO_4^{2-}, NO_3^-, and NH_4^+ concentrations compared with samples associated with South Continental and North/Center Continental air masses. A similar trend was observed for other minor anthropogenic $PM_{2.5}$ constituents, including Zn, Sb, Se, and As.

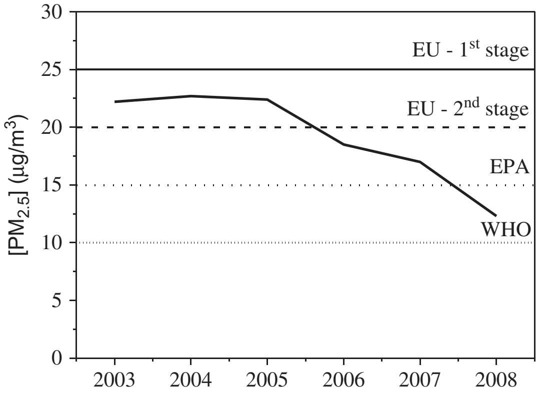

FIGURE 2. $PM_{2.5}$ concentrations measured in the centre of Lisbon from 2003 to 2008 by APA. Annual limit values established by EU, EPA and WHO. Values in μg/m^3.

Source Apportionment

PCA applied to $PM_{2.5}$ particulate species identified 5 main chemical profiles sources, which accounted for 81% of the total variance. The results from the PCA performed on the data set are summarized in Table 2. Only elements with factor loadings >0.2 are shown. Interpretation of source profiles is mostly based on elements with factor loadings >0.6 considered as tracers of the different sources. The first principal component (PC) represented soil contribution, given that it presents high factor loadings for Fe, La, Sc, and nonsoluble K (calculated as K-K^+), which are typical soil elements (Almeida et al., 2008). Soil enrichment factors considering Sc as a crustal reference element and Mason and Moore soil composition (FE_{Sc}= $([X]/[Sc])_{PM}/([X]/[Sc])_{crust}$; Mason and Moore, 1982) were determined for Fe (average = 17), La (average = 19), and K (average = 54) (Figure 3). These results confirmed that Fe and La had a crustal origin with a negligible anthropogenic source to the atmosphere. K presented higher enrichment factors showing that other sources contributed to its emission. PCA results showed an association of K with different sources depending on its solubility: (a) Mineral aerosol was principally associated with nonsoluble K, whereas (b) K^+ presented a strong correlation with PC2.

K^+, NO_3^-, Zn, Br, Sb, and As correlated with PC2, which represented traffic emissions. Previous studies demonstrated an association between NO_3^- and K^+ with road vehicles exhaust and Zn and Sb with tires and brake wear (Almeida et al., 2009). Enrichment factors for Zn, Br, Sb, and As suggested a significant fraction of these elements originated from noncrustal sources.

In an attempt to quantify additional aerosol input by road traffic, roadside impact (RI) factors were calculated (Oliveira et al., 2010). This study defined RI as the fractional difference between the concentrations at the roadside (R) and urban background (UB) sites (RI = (R – UB)/R). For that, $PM_{2.5}$ data from the APA roadside station (Entrecampos) and from the background station (Olivais) for 2007 were used. An average RI of 9.6% was found for $PM_{2.5}$ where RI factors were higher on weekdays (10%) than weekends (3.7%).

In the Lisbon urban area, road traffic is markedly reduced on weekends due to the absence of commuter traffic and heavy-weight vehicles transporting goods and materials. Therefore, a weekday impact (WI) factor was also determined as a contribution to quantify additional particles input by traffic (Figure 4). WI was defined as the fractional difference between $PM_{2.5}$ and its constituent concentrations measured on weekday (W) and weekend (WE) (WI = (W – WE)/W). The highest WI values were calculated for the elements associated

TABLE 2. Varimax normalized rotated factor loading and communalities obtained in PCA applied to $PM_{2.5}$

	PC1 Soil	PC2 Vehicles	PC3 Sea	PC4 Secondary A	PC5 Ca source	Comun.
As	0.58	**0.61**				0.78
Br		**0.70**	0.27			0.63
Co	**0.76**	0.40		0.21		0.81
Fe	**0.96**					0.95
La	**0.97**					0.94
Sb	0.32	**0.61**				0.45
Sc	**0.94**					0.95
Se				**0.72**		0.37
Zn	0.24	**0.73**	−0.24			0.66
Cl^-	0.28	0.31	**0.76**	−0.23	−0.22	0.77
NO_3^-		**0.86**				0.87
SO_4^{2-}				**0.94**		0.90
Na^+			**0.95**			0.95
NH_4^+	0.25	0.52		0.71	−0.21	0.93
K^+		**0.91**				0.80
Mg^{2+}			**0.93**			0.95
Ca^{2+}					**0.95**	0.67
K, nonsoluble	**0.83**					0.77
Eigenvalues	4.71	3.99	2.55	2.12	1.20	14.50
Percent total variance explained	26.2	22.0	14.2	11.7	6.7	80.80

Only factor loadings with absolute values greater than 0.2 are presented and factor loadings with absolute values greater than 0.60 are presented in bold.

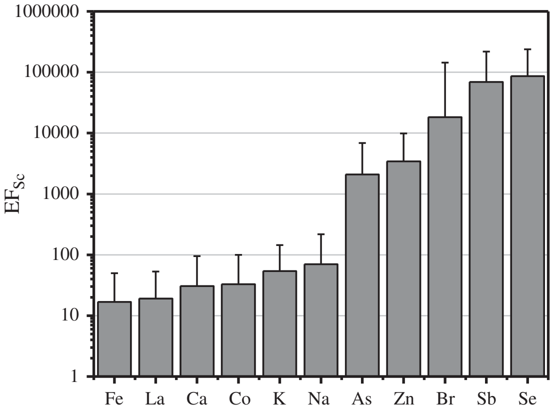

FIGURE 3. Enrichment factor using Sc as a reference element and Mason and Moore (1982) soil composition.

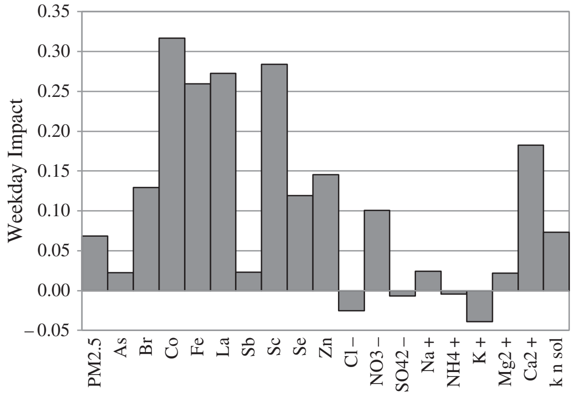

FIGURE 4. Weekday Impact factor (WI=(W-WE)/W).

with soil including Co, Fe, La, Sc, and Ca^{2+} (WI > 15%). This variability between weekdays shows that most of the soil-derived dust is produced by anthropogenic activities, presumably resulting from road dust resuspension by road traffic (Almeida et al., 2006a). Zn that is predominantly generated from tires and motor oils and NO_3^- that originates from vehicle exhaust had WI factors of 14 and 10%, respectively.

PC3 presented a strong correlation with Na^+, Mg^{2+}, and Cl^- and representing marine aerosol emissions (Almeida et al., 2006c). Figure 5 shows the relationship between Mg^{2+} and Na^+. The line represents bulk seawater weight concentration ratio ($Mg^{2+}/ Na^+ = 0.12$) (Bowen, 1979). It is evident that Mg^{2+} is associated with Na^+. The slope of the regression line (0.12) compares quite well with Mg^{2+}/Na^+ ratio for bulk seawater, revealing a common origin in the sea.

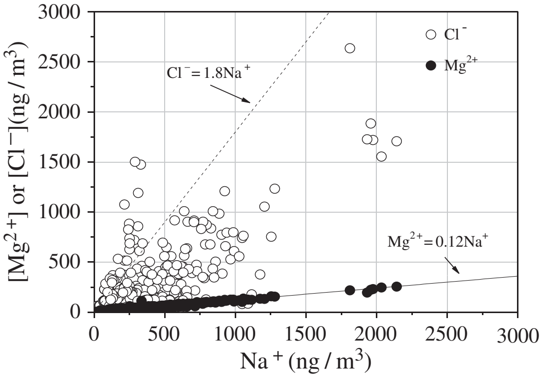

FIGURE 5. Relationship between Mg^{2+}, Cl^- and Na^+. Mg^{2+}/Na^+ (__) and Cl^-/Na^+ (—) ratios for sea water (Bowen, 1979).

The association between Cl^- and Na^+ suggests an unstable relationship between these elements. Nearly all points were located below the bulk seawater ratio line. This deficit was suggested to be the result of 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 formation of NH_4Cl from gaseous precursors (Almeida et al., 2006b).

SO_4^{2-} and NH_4^+, which are generated from gas to particle conversion processes from SO_2 oxidation and NH_3 neutralization (Almeida et al., 2006c), were the main compounds defined as the fourth PC. Figure 6 shows that SO_4^{2-} and NH_4^+ concentrations presented a correlation, which indicates that SO_4^{2-} was mainly present as $(NH_4)_2SO_4$ and/or NH_4HSO_4. PC5 correlated with Ca^{2+}. This element is associated with the cement industry emissions and in Lisbon may also result from calcareous rocks used for sidewalk coating. The average enrichment factor for this ion was 31, showing a small enrichment in relation to soil composition.

Source Contribution

Source contributions to $PM_{2.5}$ were investigated by means of MLRA. The sum of the estimated source contributions corresponds to the modeled $PM_{2.5}$ concentrations. Figure 7

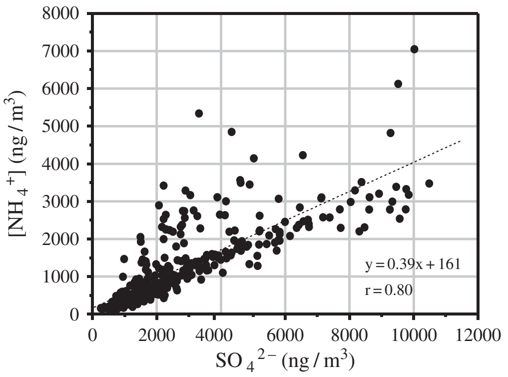

FIGURE 6. Relation between SO_4^{2-} and NH_4^+ and Na^+ (— linear regression).

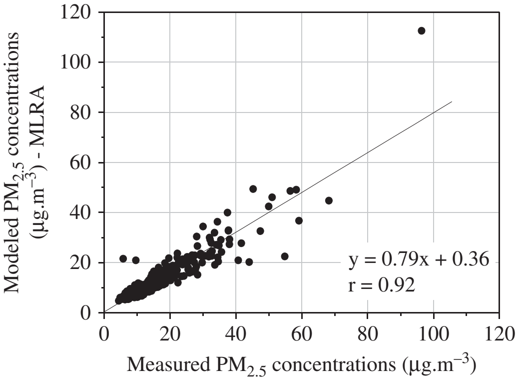

FIGURE 7. Relationship between $PM_{2.5}$ concentration calculated by PCA/MLRA and determined by gravimetry.

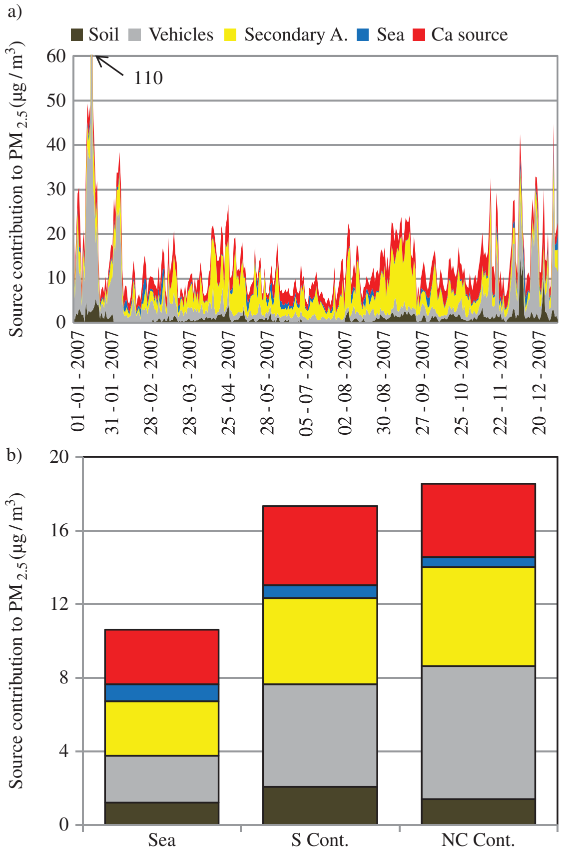

FIGURE 8. Source contribution for the modelled total $PM_{2.5}$ mass concentration (a) and discriminated by air mass type (Sea – maritime air masses; S. Cont – South Continental air masses; N/C Cont – North Centre Continental air masses) (b). Values in $\mu g/m^3$ (color figure available online).

provides evidence of good correlation between modeled and gravimetric $PM_{2.5}$ results with an *r* value equal to .92. However, the slope shows that approximately 20% of mass was not explained by the model.

The daily absolute and relative sources contributions for modeled $PM_{2.5}$ are presented Figure 8a and Figure 9a, respectively. These figures show that the largest contribution to $PM_{2.5}$ total mass were from the secondary aerosol (32%) and vehicle exhaust (30%). Mineral aerosol from soil contributes 9%, marine aerosol 5%, and Ca source 24%.

Figure 9 shows that source contribution illustrated seasonality characterized by higher contributions of secondary aerosol (48%) during summer/spring, due to the photochemical reactions, and that higher vehicles emissions (42%) contributions during winter/autumn were associated with the preferential formation of ammonium nitrate at lower winter temperatures. The average source contributions were calculated for the main types of air masses trajectories. The results presented in Figure 8b and Table 3 indicate that air mass trajectories exerted a major influence on $PM_{2.5}$ concentrations. For maritime samples the mean contributions of secondary aerosols, vehicles, soil, and Ca sources were significantly lower compared with samples associated with South Continental and North/Center Continental air masses trajectories. The contribution of the sea for $PM_{2.5}$ was not significantly higher during the maritime air mass trajectories. This fact is probably due to the higher contribution of this source to the coarse PM fraction.

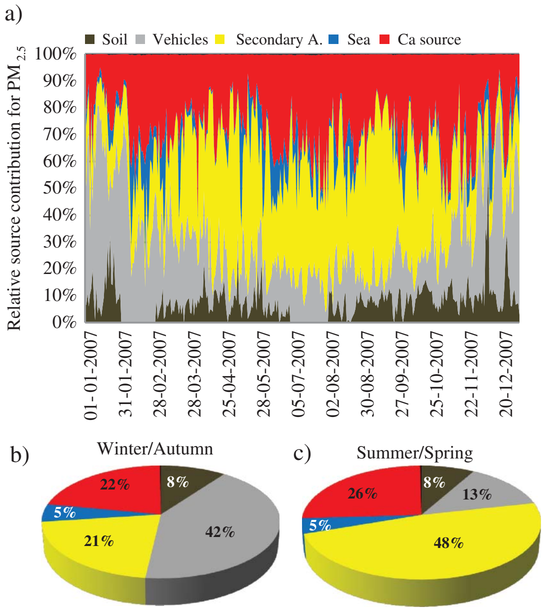

FIGURE 9. Relative source contribution for the modelled total $PM_{2.5}$ mass concentration (a); Average relative source contribution to $PM_{2.5}$ mass concentration during Winter/Autumn (b) and Summer/Spring (c) (color figure available online).

TABLE 3. *p* Value using Mann-Whitney *U*-test to assess the differences associated with each air mass trajectories in $PM_{2.5}$ total concentration and in the source contribution (significant differences marked in bold for $p < 0.05$)

	Sea vs. S Cont.	Sea vs. NC Cont.	S Cont. vs NC Cont.
$PM_{2.5}$	**0.000**	**0.000**	0.514
PC1 - Soil	**0.001**	**0.000**	0.274
PC2 - Vehicles	**0.000**	**0.003**	0.499
PC3 - Sea	0.137	**0.000**	0.151
PC4 – Secondary A.	**0.000**	**0.000**	0.290
PC5 - Ca source	**0.001**	**0.000**	0.971

CONCLUSIONS

In this study a chemical characterization of $PM_{2.5}$ sampled in Lisbon during the year 2007 was made and the main conclusions may be summarized as follows:

1. Five main groups of sources were identified: secondary aerosols, traffic, calcium, soil, and sea.
2. The largest contribution to $PM_{2.5}$ total mass was secondary aerosol and vehicle exhaust.
3. The contribution of identified anthropogenic sources to $PM_{2.5}$ was significantly lower for maritime samples.
4. The geographic position of Lisbon, on the Western European Coast, exerts a major influence on $PM_{2.5}$ concentrations. Maritime air mass trajectories are usually associated with transport of cleaner air masses from the Atlantic Ocean and with better dispersion conditions of pollutants coming from the industrial area. These conditions promote a lower contribution from anthropogenic sources.

REFERENCES

Almeida, S. M., Reis, M. A., Freitas, M. C., and Pio, C. A. 2003a. Quality assurance in elemental analysis of airborne particles. *Nucl. Instrum. Methods Phys. Res. B* 207: 434–446.

Almeida, S. M., Freitas, M. C., Reis, M. A., and Pio, C. A. 2003b. Quality assessment on airborne particulate matter of k_0-INAA. *J. Radioanal. Nucl. Chem*. 257: 609–613.

Almeida, S. M., Pio, C. A., Freitas, M. C., Reis, M. A., and Trancoso, M. A. 2005. Source apportionment of fine and coarse particulate matter in a sub-urban area at the western European coast. *Atmos. Environ*. 39: 3127–3138.

Almeida, S. M., Pio, C. A., Freitas, M. C., Reis, M. A., and Trancoso, M. A. 2006a. Source apportionment of atmospheric urban aerosol based on weekdays/weekend variability: Evaluation of road re-suspended dust contribution. *Atmos. Environ*. 40: 2058–2067.

Almeida, S. M., Freitas, M. C., Reis, M. A., Pio, C. A., and Trancoso, M. A. 2006b. Combined application of multielement analysis—k_0-INAA and PIXE—and classical techniques for source apportionment in aerosol studies. *Nucl. Instrum. Methods Phys. Res. A* 564: 752–760.

Almeida, S. M., Pio, C. A., Freitas, M. C., Reis, M. A., and Trancoso, M. A. 2006c. Approaching $PM_{2.5}$ and $PM_{2.5-10}$ source apportionment by mass balance analysis, principal component analysis and particle size distribution. *Sci. Total Environ*. 368: 663–674.

Almeida, S. M., Freitas, M. C., and Pio, C. A. *2008*. Neutron activation analysis for identification of African mineral dust transport. *J. Radioanal. Nucl. Chem*. 276: 161–165.

Almeida, S. M., Freitas, M. C., Repolho, C., Dionísio, I., Dung, H. M., Caseiro, A., Alves, C., Pio, C. A., and Pacheco, A. M. G. 2009. Characterizing air particulate matter composition and sources in Lisbon, Portugal. *J. Radioanal. Nucl. Chem*. 281: 215–218.

Amann, M., Bertok, I., Cabala, R., Cofala, J., Heyes, C., and Gyarfas, F. 2005. *CAFE scenario analysis report no 4. Target setting approaches for cost-effective reductions of population exposure to fine particulate matter in Europe*. Luxemburg, Austria: International Institute for Applied Systems Analysis.

Bowen, H. J. M. 1979. *Environmental Chemistry of the Elements*. London, UK: Academic Press.

Bowen, H. J. M., and Gibbons, D., 1963. *Radioactivation analysis*. Oxford, UK: Clarendon.

Chow, J. C., and Watson, J. G., 1999. Ion chromatography in elemental analysis of airborne particles, elemental analysis of airborne particles. In *Advances in environmental, industrial and process control technologies*, ed. S. Landsberger and M. Creatchman, vol. 1, 97–137. Gordon and Breach Sciences Publishers, Tennessee, USA.

Cohen, A. J., Anderson, H. R., Ostra, B., Pandey, K. D., Krzyzanowski, M., Kunzli, N., Gutschmidt, K., Pope, A., Romieu, I., Samet, J. M., and Smith, K. 2005. The global burden of disese due to outdoor air pollution. *J. Toxicol. Environ. Health A* 68: 1–7.

De Corte, F. 1987. *The k_0-standardization method—A move to the optimization of neutron activation analysis*. Agregé Thesis, Gent University, Belgium.

Draxler, R., Stunder, B., Rolph, G., Stein, A., Taylor, A., 2009. *HYSPLIT4 User's Guide*. Revision January 2009. NOAA Air Resources Laboratory. Available at http://www.arl.noaa.gov/documents/reports/hysplit_user_guide.pdf.

European Union. 2008. Official Journal of the European Union. Directive 2008/50 CE of the European Parliament and Council of 21 May 2008 on ambient air quality and cleaner air for Europe. 11 June 2008.L152/1–L152/44.

Ghio, A. J., Carraway, M. S., and Madden, M. C. 2012. Composition of air pollution particles and oxidative stress cells, tissues and living systems. *J. Toxicol. Environ Health B* 15: 1–21.

Krewski, D., Burnett, R. T., Jerrett, M., Pope, A., Rainham, D. G., Calle, E. E., Thurston, G. D., and Thun, M. 2004. Mortality and long-term exposure to ambient air pollution: Ongoing analyses based on the American Cancer Society cohort. *J. Toxicol. Environ. Health A* 68: 1093–1109.

Mason, B., and Moore, C. B., 1982. *Principles of geochemistry*, 46. New York, NY: Wiley.

Oliveira, C., Pio, C. A., Caseiro, A., Santos, P., Nunes, T., Mao, H., Luahana, L., and Sokhi, R. 2010. Road traffic impact on urban atmospheric aerossol loading at Oporto, Portugal. *Atmos. Environ*. 44: 3147–3158.

Pérez, N., Pey, J., Querol, X., Alastuey, A., López, J. M., and Viana, M., 2008. Partitioning of major and trace components in PM_{10}–$PM_{2.5}$–PM_1 at an urban site in Southern Europe. *Atmos. Environ*. 42: 1677–1691.

Pio, C. A., and Lopes, D. A. 1998. Chlorine loss from marine aerosol in a coastal atmosphere. *J. Geophys. Res*. 103: 25263–25272.

Pope, C., Burnett, R., Thun, M., Calle, E., Frewski, D., Ito, K., and Thurston, G.D. (2002). Lung cancer, cardiopulmonary mortality, and long-term exposure to fine particulate air pollution. *J. Am. Med. Assoc*. 28: 1132–1141.

Putaud, J.-P., Dingenen, R. V., Alastuey, A., Bauer, H., Birmili, W., Cyrys, J., Flentje, H., Fuzzi, S., Gehrig, R., Hansson, H. C., Harrison, R. M., Herrmann, H., Hitzenberger, R., Hüglin, C., Jones, A.

M., Kasper-Giebl, A., Kiss, G., Kousa, A., Kuhlbusch, T. A. J., Löschau, G., Maenhaut, W., Molnar, A., Moreno, T., Pekkanen, J., Perrino, C., Pitz, M., Puxbaum, H., Querol, X., Rodriguez, S., Salma, I., Schwarz, J., Smolik, J., Schneider, J., Spindler, G., ten Brink, H., Tursic, J., Viana, M., Wiedensohler, A., and Raes, F., 2010. A European aerosol phenomenology—3: Physical and chemical characteristics of particulate matter from 60 rural, urban, and kerbside sites across Europe. *Atmos. Environ*. 44: 1308–1320.

Samet, J., and Krewski, D. 2007. Health effects associated with exposure to ambient air pollution. *J. Toxicol. Environ. Health A*: 227–242.

U.S. Environmental Protection Agency. 2006. PM standards revision 2006. Available at http://epa.gov/pm/naaqsrev2006.html.

World Health Organization. 2006. WHO air quality guidelines for particulate matter, ozone, nitrogen dioxide and sulfur dioxide. Global update 2005. WHO/SDE/PHE/EH/06.02. Available at http://whqlibdoc.who.int/hq/2006/WHO_SDE_PHE_OEH_06.02_eng.pdf