

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

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Abstract

Lisbon is the largest urban area in the Western European coast. Due to this geographical position, the Atlantic Ocean is an important source of particles and plays an important role in many atmospheric processes. The main objectives of this work were 1) to perform a chemical characterization of PM_{2.5} sampled in Lisbon, 2) to identify the main sources of particles and to determine their contribution to this urban area and 3) to assess the impact of maritime air mass trajectories on the concentration and composition of respirable particles sampled in Lisbon. During 2007, PM_{2.5} was collected on a daily basis in the centre of Lisbon with a Partisol sampler. The exposed teflon filters were measured by gravimetry and were cut into two parts: one was analysed by Instrumental Neutron Activation Analysis and the other by Ion Chromatography. Principal Component Analysis and Multilinear Regression Analysis were used to identify possible sources of PM_{2.5} and to determine their mass contribution. Five main groups of sources were identified: secondary aerosols, traffic, a source of calcium, soil and sea. Four days backward trajectories, ending in Lisbon, at the starting sampling time were calculated with the Hysplit Model. Results showed that maritime transport scenarios were very frequent. These episodes were characterized by a significant decrease of anthropogenic aerosol concentrations and had a significant role on the air quality from this urban area.

Keywords - Urban Aerosol, Air Mass Trajectories, PM_{2.5}, Sea, Source Apportionment.

1 INTRODUCTION

The Clean Air for Europe programme estimated that approximately 350 thousand premature deaths occur annually due to exposure to ambient air fine particulate matter (PM_{2.5}) [1]. The problem of air pollution with PM_{2.5} is especially important where dense urban populations are exposed to anthropogenic emissions. This fact led policies makers to legislate more and more stringent emission and air pollution limit levels. Therefore, PM_{2.5} concentrations are expected to decrease significantly over the next decades. 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 mitigation actions to achieve these legislated levels and to reduce adverse health effects.

In such areas, traffic emissions is the principal source of particles (rich in heavy metals) not only due to vehicles exhaust but also due to resuspension of particles from the road surface [2]. In addition to the local and regional particulate matter (PM)

sources, the levels and the physical and chemical properties of ambient air PM depend not only on climatology (mainly temperature, humidity, photochemistry, resuspension of soil particles, rain scavenging potential, re-circulation of air masses, dispersive atmospheric conditions) but also on the geography (mainly proximity to the coast, topography, soil cover and proximity to arid zones) of a given region [3]. Therefore, wide variations in PM levels and characteristics may be expected when considering different European locations [4].

Due to the geographical position of Lisbon, on the extreme southwest of Europe, and to 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, maritime influence is very important for this urban aerosol. The main objectives of this work were 1) to identify sources and quantify their contributions to PM_{2.5} and 2) to assess the impact of the geographical localization of Lisbon in the concentration and composition of respirable particles.

2 EXPERIMENTAL

2.1 Site description

During 2007, PM_{2.5} was sampled in Lisbon. Lisbon is the capital and largest city of Portugal, with a

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population of 564,657 within its administrative limits on a land area of 84.8 km². The urban area of Lisbon extends beyond the administrative city limits with a population of 2.4 million on an area of 958 km². 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 centre of Lisbon (38°44'N; -9°8'W), 4 km from the Tagus Estuary valley and 20 km from the Atlantic Ocean (Fig. 1). It is surrounded by high density traffic roads.

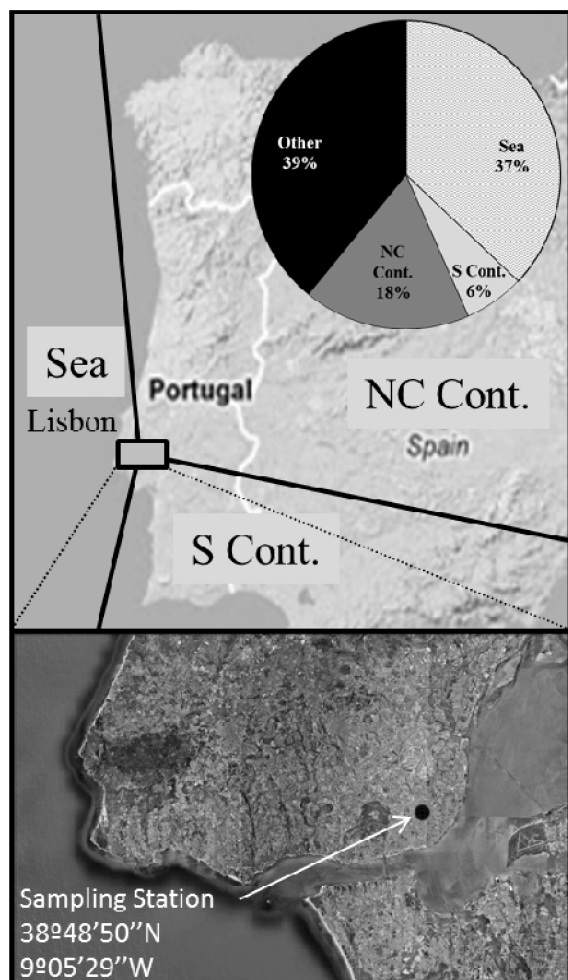


Fig. 1. Sampling localization and air mass trajectories sectors categorization and frequency (Sea – maritime air masses; S. Cont – South Continental air masses; N/C Cont – North Centre Continental air masses).

2.2 APM sampling and analysis

PM_{2.5} was collected on a daily basis during 24 h periods. Sampling was done with a Partisol sampler operating at a flow rate of 16 l.min⁻¹. Aerosol samples were collected on Teflon® filters with 47 mm diameter.

The filter loads were measured by gravimetry using a Mettler Toledo balance with 0.1 µg readability placed in a controlled clean room (class 10,000). Filter weight before and after sampling was obtained as the average of three measurements in agreeing by less than 5 µg.

The exposed filters were cut into two parts: one was analysed by k₀ based Instrumental Neutron Activation Analysis (k₀-INAA) [5,6] for elemental characterization and the other was analysed by Ion Chromatography [7] for water soluble ions determination.

For elemental analysis, filters halves were rolled up and put into a polyethylene container and irradiated for 5 hours at a thermal neutron flux of 1.03×10¹³ cm⁻²s⁻¹ in the 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 weeks. The k₀-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, Rb, Ag, Cd, Sb, Cs, Ba, La, Ce, Sm, Eu, Tb, Yb, Hf, Ir, Hg, Th, U and Mn were determined in PM_{2.5} filters. 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 k₀-INAA. Results were reproducible to within 5–15%, providing strong support for the validity of the analytical techniques [8,9]. The accuracy of analytical methods was evaluated with NIST filter standards, revealing results with an agreement of ±10% [10].

For water-soluble ions determination, filters halves were extracted with distilled deionized water by ultrasonic and mechanical shaking and filtered through a pre-washed Whatman 42 filter. The aqueous extract was analysed by Ion Chromatography to determine the concentrations of Cl⁻, NO₃⁻, SO₄²⁻, Ca²⁺, Mg²⁺, Na⁺ and K⁺.

Blank 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.

2.3 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 (<http://www.qualar.org>).

2.4 Air mass trajectories, PCA and MLRA procedures

For each starting sample date three days backward trajectories, ending in Lisbon, were calculated with the Hysplit Model [11] at 50, 500 and 1000 m height and using the vertical velocity option. According to the backward trajectories, air masses arriving in Lisbon during the sampling campaign were classified into three main groups: Sea - Maritime air masses – if backward trajectories indicated an ocean origin, without continental contamination, during the previous 3 days; S Cont. - South Continental air masses – if backward trajectories indicated an African or Southern Europe origin, NC Cont.-North/Centre Continental air masses - if backward trajectories indicated an origin in the North or Centre of Europe. Samples associated with ocean origin trajectories, with a final re-circulation through the Iberian Peninsula or trajectories indicated an European origin with a final re-circulation through the ocean were considered as “other” in Fig. 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. [12].

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 were retained for PCA analysis.

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 PM_{2.5} total mass concentrations and as independent variables the specie 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 allowed for the interpretation of the seasonal patterns of the source contributions.

The non-parametric Mann-Whitney U test was used to compare the contribution of sources for each air mass trajectory type. Statistical significance refers to $p < 0.05$. Statistical calculations were performed using STATISTICA software.

3 RESULTS AND DISCUSSION

3.1 PM_{2.5} concentrations

Fig. 1 shows the frequency of the air masses trajectories that affected Lisbon during the year 2007. It is clear that Lisbon aerosol was greatly

affected by maritime aerosol: either by pure sea trajectories (37%) or by ocean origin trajectories, with a final re-circulation through the Iberian Peninsula and trajectories indicated an European origin with a final re-circulation through the ocean (39%). In order to assess the influence of the different air mass trajectories for the aerosol, Table 1 present the average concentrations of PM_{2.5} constituents not only for all samples but also differentiated by air mass trajectories type.

Table 1: Average 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/Centre Continental).

	All (n=348)	Sea (n=128)	S Cont. (n=22)	NC Cont. (n=61)
PM _{2.5}	18000	13000	22000	23000
SO ₄ ²⁻	2800	1800	2900	3300
NO ₃ ⁻	1600	910	2000	2600
NH ₄ ⁺	1300	760	1300	1700
Na	390	540	320	220
Cl	290	400	300	220
K	220	140	340	310
Ca ²⁺	160	140	200	190
Fe	160	140	240	160
Mg ²⁺	46	64	40	27
Zn	32	21	38	45
Br	4.9	5.7	3.1	4.6
Sb	1.8	1.4	2.3	2.7
Se	0.73	0.63	0.69	0.76
As	0.61	0.42	1.17	0.72
Co	0.16	0.15	0.16	0.16
La	0.13	0.11	0.19	0.13
Sc	0.032	0.064	0.043	0.014

In 2007 the average concentration measured in the centre of Lisbon was 18 µg.m⁻³. Comparing 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 [4]. Table 1 shows that samples associated with air mass trajectories providing from the sea presented significantly lower PM_{2.5} concentrations comparing with samples associated with South Continental ($p=0.00$) and North/Centre Continental ($p=0.00$) 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. Stage 1 indicates that the annual limit value for this pollutant is $25 \mu\text{g}\cdot\text{m}^{-3}$ 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 $20 \mu\text{g}\cdot\text{m}^{-3}$ and is to be attained by 1 January 2020. Though the Directive itself indicates that these indicative limit values will be reviewed by the Commission in 2013 in the light of further information on health and environmental effects, technical feasibility and experience of the target value ($25 \mu\text{g}\cdot\text{m}^{-3}$ at 1 January 2010) [13]. Both target values were not exceeded during 2007.

The United States Environmental Protection Agency (EPA) sets the permitted annual maximum concentration at $15 \mu\text{g}\cdot\text{m}^{-3}$ [14]. The WHO established an annual average concentration of $10 \mu\text{g}\cdot\text{m}^{-3}$ as the long-term guideline value for $\text{PM}_{2.5}$ [15]. This value represents the lowest value at which total, cardiopulmonary and lung cancer mortality have been shown to increase with more than 95% confidence in response to long-term exposure to $\text{PM}_{2.5}$ [16]. In 2007, both $\text{PM}_{2.5}$ EPA limit value and WHO guideline were exceeded.

Fig. 2 shows the $\text{PM}_{2.5}$ annual average concentrations measured by the Portuguese Environment Agency (APA) Air Quality Monitoring Network since 2003 to 2008. Besides the significant decrease of $\text{PM}_{2.5}$ concentrations since 2003, in order to achieve the ambitious goal proposed by WHO and to decline the levels of $\text{PM}_{2.5}$, the country has to adopt increasingly stringent set of standards, tracking progress through the monitoring of emission reductions.

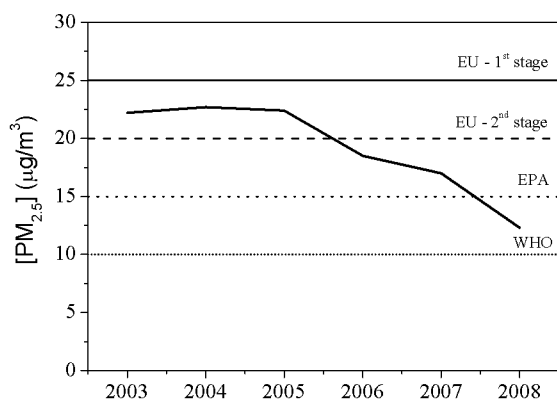


Fig. 2. $\text{PM}_{2.5}$ concentrations measured in the centre of Lisbon from 2003 to 2008 by APA. Annual limit values established by EU, EPA and WHO. Values in $\mu\text{g}/\text{m}^3$.

The major species (concentrations generally higher than $1 \mu\text{g}\cdot\text{m}^{-3}$) measured in $\text{PM}_{2.5}$ 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 providing from the sea presented significantly lower SO_4^{2-} , NO_3^- and NH_4^+ concentrations comparing with samples associated

with South Continental and North/Centre Continental air masses ($p < 0.02$). Same trend was observed for the other minor anthropogenic $\text{PM}_{2.5}$ constituents (Zn, Sb, Se, As).

3.2 Source apportionment

PCA applied to $\text{PM}_{2.5}$ particulate species identified five main chemical profiles sources, which accounted for 81% of the total variance. The results from the PCA performed on the dataset are summarised in Table 2. Only elements with factor loadings > 0.20 are shown. Interpretation of source profiles is mostly based on elements with factor loadings > 0.60 considered as tracers of the different sources.

Table 2: Varimax normalized rotated factor loading and communalities obtained in PCA applied to $\text{PM}_{2.5}$.

	PC1 Soil	PC2 Vehicles	PC3 Sea	PC4 Secondary A	PC5 Casource	Commun.
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 - non soluble	0.83					0.77
Eigenvalues	4.71	3.99	2.55	2.12	1.20	14.50
% total var. expl.	26.2	22.0	14.2	11.7	6.7	80.80

The first principal component (PC) represented the soil contribution, given that it presents high factor loadings for Fe, La, Sc and non-soluble K which are typical soil elements [17]. Soil enrichment factors - considering Sc as a crustal reference element and Mason and Moore soil composition ($\text{FE}_{\text{Sc}} = ([X]/[\text{Sc}]_{\text{PM}})/([X]/[\text{Sc}]_{\text{crust}})$ [18] - were determined for Fe (average = 2.2), La (average = 2.9) and K (average = 5.8) (Fig. 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 for its emission. ACP results showed an association of K with different sources depending on its solubility: a) mineral aerosol was principally associated with non-soluble K whereas b) K^+ presented a strong correlation with PC2.

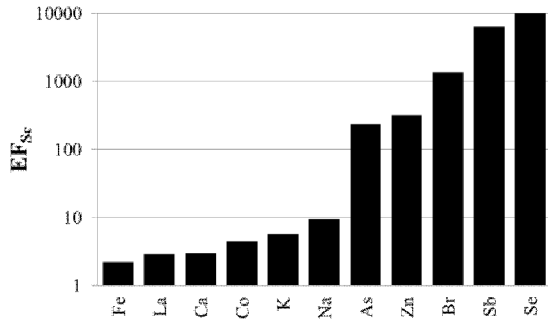


Fig. 3. Enrichment factor using Sc as a reference element and Mason and Moore [18] soil composition.

K^+ , NO_3^- , Zn, Br, Sb and As correlated with PC2 that represented traffic emissions. Previous studies have already showed an association between NO_3^- and K^+ with road vehicles exhaust and Zn and Sb with tyres and brake wear [19,20]. The enrichment factors for Zn, Br, Sb and As suggested that a significant fraction of these elements was contributed by non-crustal sources.

As an attempt to quantify the additional aerosol input by road traffic, Roadside Impact (RI) factors were calculated according to Oliveira et al. [21]. This work 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 APA roadside station (Entrecampos) and from background station (Olivais) for 2007 were used. An average RI of 9.6% was determined for $PM_{2.5}$ being the RI factors higher at weekdays (10%) than at weekends (3.7%).

In the Lisbon urban area, road traffic is strongly reduced at 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 (Fig. 4). WI was defined as the fractional difference between the $PM_{2.5}$ and its constituents concentrations measured at weekday (W) and weekend (WE) ($WI=(W-WE)/W$). The highest WI were calculated for the elements associated with soil - 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 re-suspension by road traffic [2]. Zn that results mainly from tyres and motor oils and NO_3^- that provide from vehicle exhaust had WI factors of 14% and 10%, respectively.

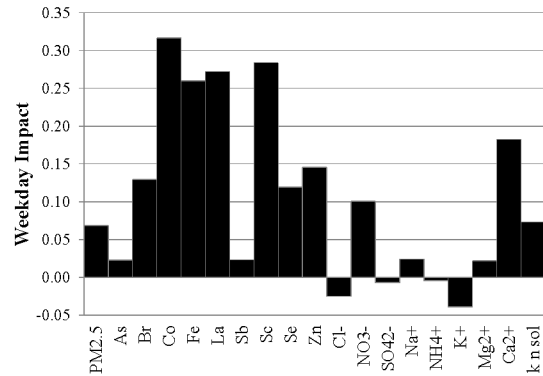


Fig. 4. Weekday Impact factor ($WI=(W-WE)/W$).

PC3 presented a strong correlation with Na^+ , Mg^{2+} , and Cl^- and represented marine aerosol emissions [22]. Fig. 5 shows the relation between Mg^{2+} and Na^+ . The line represents bulk sea water weight concentration ratio ($Mg^{2+}/Na^+=0.12$) [23]. It is evident that Mg^{2+} is strongly associated with Na^+ . The slope of the regression line (0.12) compares quite well with Mg^{2+}/Na^+ ratio for bulk sea-water, revealing a common origin in the sea.

The relation between Cl^- and Na^+ 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 [24]. 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 [10].

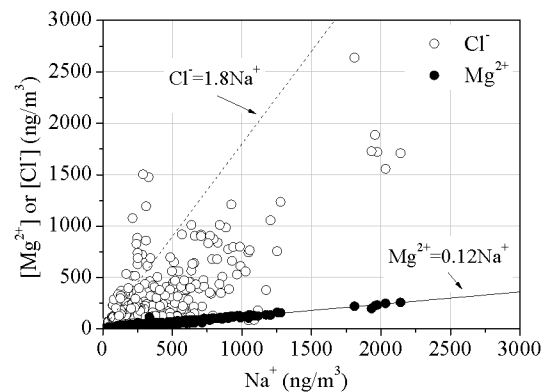


Fig. 5. Relation between Mg^{2+} , Cl^- and Na^+ . Mg^{2+}/Na^+ (—) and Cl^-/Na^+ (---) ratios for sea water [20].

SO_4^{2-} and NH_4^+ - which derive from gas to particle conversion processes from SO_2 oxidation and NH_3 neutralization [22] - were the main compounds defining the fourth PC. Fig. 6 shows that SO_4^{2-} and NH_4^+ concentrations presented a strong correlation ($r=0.80$, slope=0.39), which indicates that SO_4^{2-} was mainly present as $(NH_4)_2SO_4$ and/or NH_4HSO_4 .

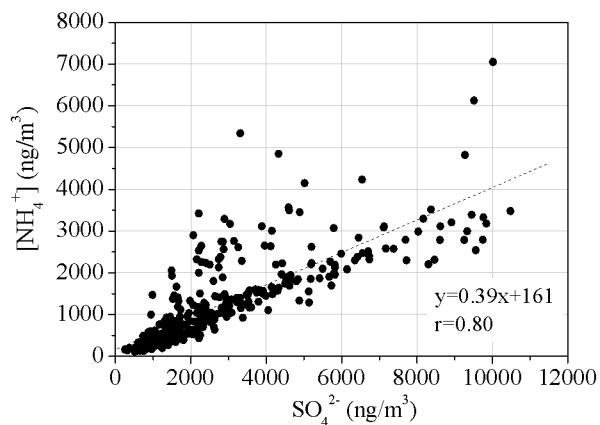


Fig. 6. Relation between SO_4^{2-} and NH_4^+ and Na^+ (---linear regression).

PC5 correlated with Ca^{2+} . This element can result from the calcareous rocks used for sidewalk coating in Lisbon. The average enrichment factor for this ion was 3 showing an association of this element with a crustal source.

3.3 Source contribution

Source contributions to $\text{PM}_{2.5}$ were carried out by means of MLRA. The sum of the estimated source contributions correspond the modelled $\text{PM}_{2.5}$ concentrations. Fig. 7 evidences the good correspondence between the modelled and the gravimetric $\text{PM}_{2.5}$ results, with r value equal to 0.92.

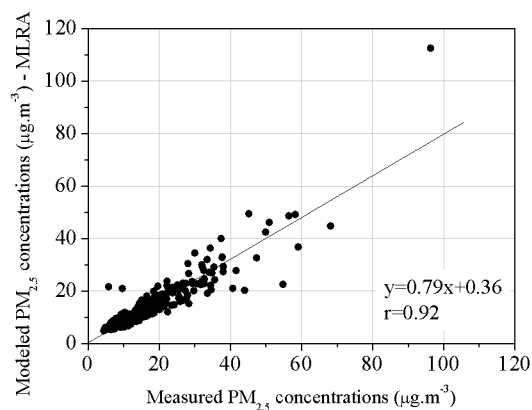


Fig. 7. Relation between $\text{PM}_{2.5}$ concentration calculated by PCA/MLRA and determined by gravimetry.

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

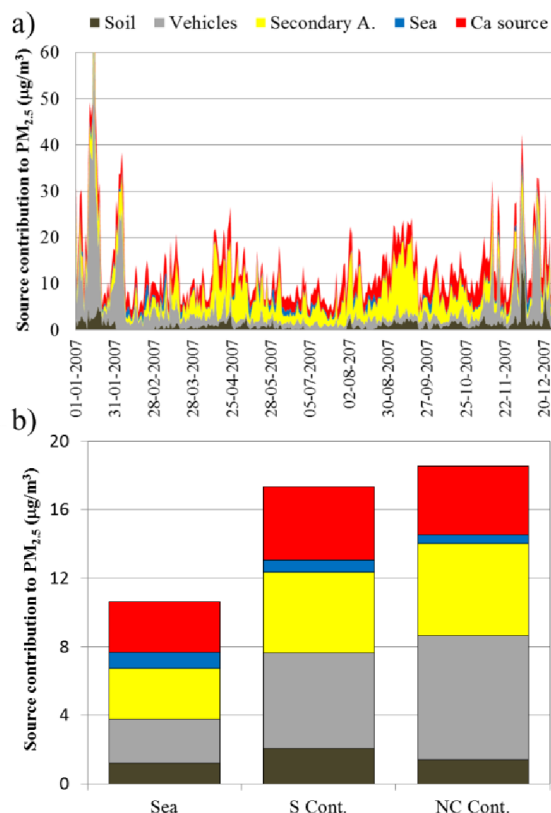


Fig. 8. Source contribution for $\text{PM}_{2.5}$ total mass concentration time series (a) and discriminated by air mass type (Sea – maritime air masses; S. Cont – South Continental air masses; N/C Cont – North Centre Continental air masses) (b). Values in $\mu\text{g}.\text{m}^{-3}$.

Fig. 9 evidences that source contribution presented seasonality, characterized by higher contributions of secondary aerosol (48%), during summer/spring, due to the photochemical reactions; and higher vehicles emissions (42%) contributions during winter/autumn, 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 Fig. 8b and Table 3 indicate that air mass trajectories exert a major influence on $\text{PM}_{2.5}$ concentrations. For maritime samples the average contribution of secondary aerosols, vehicles, soil and the Ca sources was significantly lower comparing with samples associated with South Continental and North/Centre Continental air masses trajectories. The contribution of the sea for $\text{PM}_{2.5}$ was not significantly higher during the maritime air mass trajectories. This fact is probably due to the higher contribution of this source for the coarse fraction.

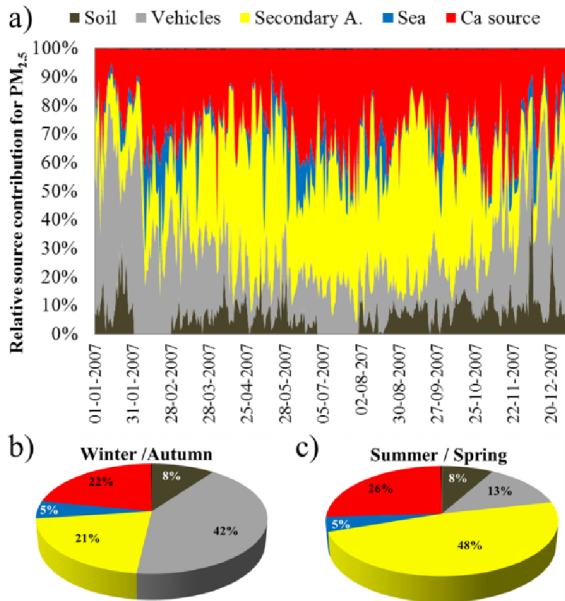


Fig. 9. Relative source contribution for $PM_{2.5}$ total mass concentration time series (a); Average relative source contribution to $PM_{2.5}$ mass concentration during Winter/Autumn (b) and Summer/Spring (c).

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

4 CONCLUSIONS

In this work 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, a source of calcium, soil and sea.
- 2) The largest contribution to $PM_{2.5}$ total mass was the secondary aerosol and vehicle exhaust.
- 3) The contribution of the identified anthropogenic sources to $PM_{2.5}$ was significantly lower for maritime samples.
- 4) The geographic position of Lisbon, in the Western European Coast, exerts a major influence on $PM_{2.5}$ concentrations. Maritime air mass trajectories 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 sources.

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REFERENCES

- [1] M. Amann, I. Bertok, R. Cabala., J. Cofala, C. Heyes, F. Gyarmas, et al., CAFE "Scenario Analysis Report No 4. Target Setting Approaches for Cost-effective Reductions of Population Exposure to Fine Particulate Matter in Europe", *International Institute for Applied Systems Analysis*, Schlossplatz 1, A-2361 Laxenburg Austria. http://www.iiasa.ac.at/rains/CAFE_files/CAFE-B-full-feb3.pdf (accessed Feb 14, 2007), 2005.
- [2] S.M. Almeida, C.A. Pio, M.C. Freitas, M.A. Reis, and M.A. Trancoso, "Source apportionment of atmospheric urban aerosol based on weekdays/weekend variability: evaluation of road Re-suspended dust contribution", *Atmospheric Environment*, vol. 40, pp. 2058–2067, 2006.
- [3] N. Pérez, J. Pey, X. Querol, A. Alastuey, J.M. López, and M. Viana, "Partitioning of major and trace components in PM_{10} - $PM_{2.5}$ - PM_1 at an urban site in Southern Europe", *Atmospheric Environment*, vol. 42, pp. 1677-1691, 2008.
- [4] J.-P. Putaud, R. V. Dingenen, A. Alastuey, H. Bauer, W. Birmili, J. Cyrys, H. Flentje, S. Fuzzi, R. Gehrig, H.C. Hansson, R.M. Harrison, H. Herrmann, R. Hitznerberger, C. Hüglin, A.M. Jones, A. Kasper-Giebl, G. Kiss, A. Kousa, T.A.J. Kuhlbusch, G. Löschau, W. Maenhaut, A. Molnar, T. Moreno, J. Pekkanen, C. Perrino, M. Pitz, H. Puxbaum, X. Querol, S. Rodriguez, I. Salma, J. Schwarz, J. Smolik, J. Schneider, G. Spindler, H. ten Brink, J. Tursic, M. Viana, A. Wiedensohler, and F. Raes, "A European aerosol

- phenomenology - 3: Physical and chemical characteristics of particulate matter from 60 rural, urban, and kerbside sites across Europe”, *Atmospheric Environment*, vol. 44, pp. 1308-1320, 2010.
- [5] H.J.M. Bowen, D. Gibbons, *Radioactivation Analysis*. Clarendon, Oxford, 1963.
- [6] F. De Corte. “The k_0 -standardization method—a move to the optimization of neutron activation analysis”, Agregé Thesis, Gent University, Belgium, 1987.
- [7] J.C. Chow, and J.G. Watson, “Ion Chromatography in elemental analysis of airborne particles”, *Elemental Analysis of Airborne Particles. Advances in Environmental, Industrial and Process Control Technologies*, S. Landsberger and M. Creatchman, eds., Gordon and Breach Sciences Publishers, vol. 1, USA, pp. 97–137, 1999.
- [8] S.M. Almeida, M.A. Reis, M.C. Freitas, and C.A. Pio, “Quality assurance in elemental analysis of airborne particles”, *Nuclear Instruments and Methods in Physics Research B*, vol. 207, pp. 434–446, 2003.
- [9] S.M. Almeida, M.C. Freitas, M.A. Reis, and C.A. Pio, “Quality assessment on airborne particulate matter of k_0 -INAA”, *Journal of Radioanalytical and Nuclear Chemistry*, vol. 257, pp. 609–613, 2003.
- [10] S.M. Almeida, M.C. Freitas, M.A. Reis, C.A. Pio, and M.A. Trancoso, “Combined application of multielement analysis - k_0 -INAA and PIXE - and classical techniques for source apportionment in aerosol studies”, *Nuclear Instruments and Methods in Physics Research A*, vol. 564, pp. 752-760, 2006.
- [11] R. R. Draxler, *Hybrid Single-Particle Lagrangian Integrated Trajectories*. Version 3.2, NOAA-ARL, 1994.
- [12] S.M. Almeida, C.A. Pio, M.C. Freitas, M.A. Reis, and M.A. Trancoso, “Source apportionment of fine and coarse particulate matter in a sub-urban area at the western European coast”, *Atmospheric Environment*, vol. 39, pp. 3127–3138, 2005.
- [13] 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.
- [14] US EPA. PM standards revision 2006. Available at: <http://epa.gov/pm/naaqsr2006.html>.
- [15] World Health Organization, “WHO air quality guidelines for particulate matter, ozone, nitrogen dioxide and sulfur dioxide”, Global update 2005–2006 WHO/SDE/PHE/EH/06.02.
- [16] C.A. Pope, R.T. Burnett, J.T. Michael, et al, “Lung cancer, cardiopulmonary mortality and long-term exposure to fine particulate air pollution”, *J American Medical Association*, vol. 287, pp. 1132–1141, 2002.
- [17] S.M. Almeida, M.C. Freitas, and C.A. Pio, “Neutron activation analysis for identification of African mineral dust transport”, *Journal of Radioanalytical and Nuclear Chemistry*, vol. 276, pp. 161-165, 2008.
- [18] B. Mason, C.B. Moore. *Principles of Geochemistry*. Wiley, New York, pp. 46, 1982.
- [19] S.M. Almeida, M.C. Freitas, C. Repolho, I. Dionísio, H.M. Dung, A. Caseiro, C. Alves, C.A. Pio, and A.M.G. Pacheco, “Characterizing air particulate matter composition and sources in Lisbon, Portugal”, *Journal of Radioanalytical and Nuclear Chemistry*, vol. 281, pp. 215-218, 2009.
- [20] S.M. Almeida, M.C. Freitas, C. Repolho, I. Dionísio, H.M. Dung, C.A. Pio, C. Alves, A. Caseiro, and A.M.G. Pacheco, “Evaluating children exposure to air pollutants for an epidemiological study”, *Journal of Radioanalytical and Nuclear Chemistry*, vol. 280, pp. 405-409, 2009.
- [21] C. Oliveira, C.A. Pio, A. Caseiro, P. Santos, T. Nunes, H.Mao, L. Luahana, and R. Sokhi, “Road traffic impact on urban atmospheric aerosol loading at Oporto, Portugal”, *Atmospheric Environment*, vol.44, pp. 3147-3158, 2010.
- [22] S.M. Almeida, C.A. Pio, M.C. Freitas, M.A. Reis, and M.A. Trancoso, “Approaching $PM_{2.5}$ and $PM_{2.5-10}$ source apportionment by mass balance analysis, principal component analysis and particle size distribution”, *Science of the Total Environment*, vol. 368, pp. 663-674, 2006.
- [23] H.J.M. Bowen, *Environmental Chemistry of the Elements*, Academic Press, London, 1979.
- [24] C.A. Pio, and D.A. Lopes, “Chlorine loss from marine aerosol in a coastal atmosphere”, *Journal of Geophysical Research*, vol. 103 (D19), pp. 25263–25272, 1998.