

Fifteen years of nuclear techniques application to suspended particulate matter studies

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Abstract Acute and chronic exposures to Airborne Particulate Matter (APM) have been linked, in epidemiological studies, to increased mortality and to a wide spectrum of respiratory and cardiovascular disorders. One factor that highly influences the toxicity of APM is its chemical composition. Nuclear Analytical Techniques (NATs) can be advantageously used in the determination of the particles element composition due to their multielement capability in association with low detection limits. Therefore, the characterization of APM by these techniques contributes to the identification of emission sources and, consequently, to the assessment of the effectiveness of the current air pollution abatement strategies. The main goal of this paper was to present the achievements obtained within 15 years of activities related with the use of NATs on the analysis of APM sampled in outdoor, indoor and industrial environments. The results presented in this work confirmed the relevance of NATs as efficient analytical techniques not only in the characterization of APM, but also in source apportionment, identification of long range transport and health assessment studies.

Keywords Nuclear techniques · INAA · PIXE · Aerosols · Environment · Industry · Indoor

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Introduction

Airborne Particulate Matter (APM) is a critical environmental health problem. When inhaled, particles affect the respiratory system and are taken up by the blood being transported throughout the body. Moreover, particles are deposited on soil, plants and water, thus further contributing to human exposure when contaminated food and water are ingested. Epidemiological studies have consistently shown an association between APM pollution and the number of deaths from cancer, cardiovascular and respiratory diseases [1, 2]. There is also evidence linking APM pollution and increases in hospital admissions for respiratory and cardiovascular diseases [3, 4]. The EU Air Quality Framework Directive (2008/50/CE) stresses the need to have a real strategy to reduce APM and establishes the “National $PM_{2.5}$ exposure reduction target for the protection of human health”.

Several parameters can influence the toxicity of the APM that is present in the outdoor, indoor or workplaces: the particle size distribution, the bulk chemical composition and the contents of trace element, acid and sulphate. However, neither the responsible component, nor the mechanism of adverse health effects is clearly known. Therefore, an accurate knowledge on the nature of the APM and, above all, on the identification of their major sources and pathways through the environment is needed to identify mitigation actions. These focused mitigation actions are essential to enforce an effective reduction of the APM and a decrease of the associated adverse health effects.

The ability of the Nuclear Analytical Techniques (NATs) to analyze solid phase samples for many elements, without the need for sample dissolution or digestion and with a high degree of sensitivity and selectivity makes

them particularly suitable for the elemental analysis of APM filters. This fact brings the issue of assessing the element APM concentrations within the scope of activities of the NANE (Neutron Activation in Environment, Nutrition and Epidemiology) group from the Nuclear and Technological Institute.

The main goal of this paper was to present the achievements obtained within 15 years of activities related with the use of NATs on the analysis of APM sampled in the outdoor, indoor and industrial environments. In order to achieve this goal, this work focused on three main research works:

- 1) The characterization of APM in an industrial-urban area located at the Western European Coast: this work was developed within the PhD thesis developed by Almeida [5] and aimed to identify APM emission sources;
- 2) The characterization of APM in two indoor environments: offices and primary schools: this work was developed within the project “*Impact of indoor on human health*” which the objective was to analyze the health risks associated with the exposure to indoor pollutants [6–12];
- 3) The characterization of particles sampled in industrial environments: this work was developed within the project “*Exhaled breath condensate: a tool for noninvasive evaluation of pollutant exposition?*” that aimed to develop the exhaled breath condensate as a human bioindicator to be applicable for professional exposure [13–17].

Experimental

APM was sampled in three different types of environment: outdoor, indoor and industrial. In the outdoor, APM was sampled in an industrial-urban area located in the North of Lisbon—Bobadela. In the indoor, $PM_{2.5}$ and $PM_{2.5-10}$ were collected in three primary schools located in Lisbon and in four offices situated in Bobadela. The industrial particles were sampled inside two lead processing industries. Industry 1 recycles batteries and Industry 2 produces batteries. Both industries are located in the North of Lisbon. Table 1 presents some details on the sampling and analytical methodologies used for the assessment of APM concentrations and composition.

Sampling equipment

Three types of sampling equipments were used to collect APM: four Gent PM_{10} samplers, a high volume sampler and a Berner Impactor.

The Gent PM_{10} samplers were equipped with a stacked filter unit, which carried, in two sequential stages, 47 mm Nuclepore polycarbonate filters, with 8 and 0.4 mm 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 2.5 and 10 μm , in the first stage, and fine particles with AD <2.5 μm in the second stage.

The high volume sampler was equipped with a Sierra PM_{10} 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. The high volume aerosol samples were collected on pre-washed and thermally treated Whatman QM-A quartz fibre filters.

APM was also collected with a Berner Impactor (Hauke LPI 30/0,06/2). The device contained 8 impaction stages with cut AD of 16, 8, 4, 2, 1, 0.5, 0.25, 0.125 and 0.0625 μm . The air was sampled at a rate of 30.8 l min⁻¹ and Nuclepore polycarbonate filters coated with Apiezon were used as the collection substrates.

Gravimetry

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 <5 %.

Chemical analysis

Samples collected in Nuclepore filters were used for elemental analysis using k_0 based Instrumental Neutron Activation Analysis (k_0 -INAA) and Particle Induced X-Ray Emission (PIXE). Details about k_0 -INAA and PIXE analysis are summarized in Table 1 and were deeply described in previous works [5, 6, 14, 16].

Exposed quartz fibre filters were used for the determination of water-soluble inorganic ions. 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 analysed by ion chromatography (Cl^- , NO_3^- and SO_4^{2-}), indophenol-blue spectrophotometry (NH_4^+), atomic absorption spectroscopy (Ca^+ , Mg^{2+} , Na^+ and K^+) and potentiometry (H^+).

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.

Table 1 Sampling and analytical methodologies applied in the assessment of environment, indoor and industrial APM

	Environment	Indoor		Industry
Sampling place	1 Urban-industrial environment–Lisbon	3 Primary schools–Lisbon	4 Offices–Lisbon	2 Lead processing industries–Lisbon
Sampling date	All year 2001	May 2009 and november 2009	March 2009	April 2009 and november 2009
Sampling time	24 h	From monday to friday	From monday to friday	Between 1 and 3 h
Equipment	1 Gent sampler 1 High volume 1 Berner impactor	1 Gent sampler	1 Gent sampler	4 Gent samplers
Gravimetry	Semi-micro-balance Micro-balance	Semi-micro-balance	Semi-micro-balance	Semi-micro-balance
Techniques	k_0 -INAA Irradiation conditions ITN Portuguese research reactor Thermal Neutron Flux : $1.2 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$ Irradiation time: 7 h Measuring condition After 2–3 days—measuring time 7–15 h After 4 weeks—measuring time 7–15 h PIXE ITN Van de Graaff accelerator 1 spectra with 1.2 MeV proton beam 1 spectra with 2.4 MeV proton beam Ion chromatography Indophenol-blue spectrophotometry Atomic absorption spectroscopy Potentiometry	k_0 -INAA Irradiation conditions ITN Portuguese research reactor Thermal neutron flux : $1.03 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$ Irradiation time: 5 h Measuring condition After 2–3 days—measuring time 7 h After 4 weeks—measuring time 7 h	k_0 -INAA Irradiation conditions ITN Portuguese research reactor Thermal neutron flux : $1.03 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$ Irradiation time: 5 h Measuring condition After 2–3 days—measuring time 7 h After 4 weeks—measuring time 7 h PIXE ITN Van de Graaff accelerator 1 spectra with 1.2 MeV proton beam 1 spectra with 2.4 MeV proton beam	k_0 -INAA Irradiation conditions ITN Portuguese research reactor Thermal neutron flux : $1.03 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$ Irradiation time: 5 h Measuring condition After 2–3 days—measuring time 7 h After 4 weeks—measuring time 7 h PIXE ITN Van de Graaff accelerator 1 spectra with 1.2 MeV proton beam 1 spectra with 2.4 MeV proton beam
Measured parameters	PM, Na, Al, Si, S, Cl, K, Ca, Sc, Ti, V, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Sb, La, Sm, Hg, Pb, SO_4^{2-} , NO_3^- , Cl^- , NH_4^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , H^+	PM, As, Ba, Br, Ca, Cr, Co, Fe, K, La, Na, Sb, Sc, Se, Sm, Zn	PM, Na, Al, Si, Cl, K, Ca, Ti, Mn, Fe, Ni, Cu, Zn, As, Br, Sb, Pb	PM, Na, Al, Si, Cl, K, Ca, Ti, Mn, Fe, Ni, Cu, Zn, As, Br, Sb, Pb

Quality assurance and quality control

Previous and during all the developed work analytical control exercises were carried out using different approaches:

- 1) Tests of reproducibility, within filters and between filters sampled with two parallel and identic sampling devices, were made. Particle species were measured 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 were given in previous works [18, 19];

- 2) The accuracy of analytical methods was evaluated with the NIST standard reference material 2783—Air particulate on filters media revealing results with an agreement of $\pm 10 \%$ [20].
- 3) In order to assess the accuracy of the methods by a comparison of INAA and PIXE, one gent collector worked in 24 h periods during 104 days. Filters were divided in three parts (controlled by weighing): one half was analysed by INAA and one quarter was analysed by PIXE. Results showed a good agreement between INAA and PIXE [18].
- 4) For INAA, the NIST standard reference material 1633a—Trace elements in coal fly ash was irradiated

simultaneously with all batch of samples. Results showed that the technique is accurate [21].

Results

APM levels in different environments: outdoor, indoor and industry

$PM_{2.5}$ and $PM_{2.5-10}$ were sampled in an industrial-urban area, in the indoor of schools and offices and inside two industries that process lead. The average levels of total mass and trace constituents measured in the studied environments are summarized in Table 2.

Results showed that the concentrations of suspended particles varied from few $\mu\text{g m}^{-3}$ up to mg m^{-3} .

As expected, the total mass concentration of particles measured inside both industries was significantly larger than the concentration measured in the environment, schools and offices. In Industry 1, the average $PM_{2.5}$ and $PM_{2.5-10}$ total mass concentrations were 420 and 1,000 $\mu\text{g m}^{-3}$, respectively. In Industry 2, it was verified that the workers exposure to particles was lower than in Industry 1, being the average $PM_{2.5}$ and $PM_{2.5-10}$ total mass concentrations 60 and 70 $\mu\text{g m}^{-3}$, respectively. These concentrations did not exceeded the limit value for respirable particles (3,000 $\mu\text{g m}^{-3}$) established by the Portuguese norm for occupational exposure limits to chemical agents NP1796.

The average $PM_{2.5}$ mass concentration at the urban industrialized area located in Lisbon was 24 $\mu\text{g m}^{-3}$. This value did not exceeded the limit value of 25 $\mu\text{g m}^{-3}$ established by the Portuguese legislation (Decreto-Lei n.º 102/2010) for $PM_{2.5}$. These observed $PM_{2.5}$ levels were mainly due to anthropogenic particles providing from local sources and from long range transport. The average $PM_{2.5-10}$ mass concentration at the same site was 16 $\mu\text{g m}^{-3}$. $PM_{2.5-10}$ reached 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 [22].

The PM_{10} average concentration (40 $\mu\text{g m}^{-3}$) corresponded to the PM_{10} limit value established by the Portuguese legislation (Decreto-Lei n.º 102/2010).

The PM_{10} maximum concentration measured inside the offices (30 $\mu\text{g m}^{-3}$) did not exceeded the limit value of 150 $\mu\text{g m}^{-3}$ established by the Portuguese legislation (Decreto-Lei n.º 79/2006) related to the indoor air quality.

In schools, the average indoor $PM_{2.5}$ and $PM_{2.5-10}$ total mass concentration was 9 and 48 $\mu\text{g m}^{-3}$, respectively. The PM_{10} indoor concentrations varied between 30 and 146 $\mu\text{g m}^{-3}$ which means that the PM_{10} concentrations did not exceed the limit value of 150 $\mu\text{g m}^{-3}$.

Statistical analysis showed that $PM_{2.5-10}$ concentrations were significantly higher in schools comparing with the offices and outdoor, indicating that coarse particles measured in classrooms have other sources than outdoor particles. Occupancy, through re-suspension of previously deposited particles and possible particle generation, strongly influences the concentration level of airborne particles in schools [6]. However, this influence decreases with particle size, reflecting the way deposition velocities vary as a function of size [6].

In the outdoor environment, $PM_{2.5}$ concentration reached significant higher levels than in offices and schools probably due to the major importance of secondary aerosols that are dominant in the fine fraction.

APM composition in different environments: outdoor, indoor and industry

As expected, Industry 1 and 2 presented significantly higher element concentrations. Consequently, despite the several decades of analytical research in outdoor and indoor air particulate matter characterization by k_0 -INAA, the determination of the chemical composition of particles in these industrial environments was not a trivial task and faced difficulties in the analytical investigations due to the complex nature of the samples. In INAA the incomplete deposition of gamma-rays in the germanium crystal due to Compton scattering elevated the spectra baseline, thus increased the background, and hindered the identification of some photopeaks. The problem was particularly important due to the high Sb contents existing in the sampled filters. The additional application of the Compton Suppression System for the analysis of these filters was successfully used in order to ascertain potential improvements on the detection limits [14].

The elements with higher expression for $PM_{2.5}$ in the combustion and refining processes in the recycling Industry (Industry 1) were Pb, Sb, Na, Cl. For $PM_{2.5-10}$, adding to the previous elements, also Fe had a contribution higher than 1 % to the total mass. For the battery production Industry (Industry 2), Pb, Al, Br, Si and Ca for $PM_{2.5}$ and Pb, Si, Ca, Na, Cl, and Al for $PM_{2.5-10}$ were the major elements. In both industries, the most represented element in $PM_{2.5}$ and $PM_{2.5-10}$ was the Pb. In these industries, Pb concentration in PM_{10} was 4×10^4 (Industry 1) and 2×10^3 (Industry 2) times higher than in offices and environment. The average Pb concentration measured in Industry 1 was 180 $\mu\text{g m}^{-3}$ for $PM_{2.5}$ and 340 $\mu\text{g m}^{-3}$ for $PM_{2.5-10}$. In this Industry, Pb concentrations exceeded the limit value (50 $\mu\text{g m}^{-3}$) established by the Portuguese NP1796 for Total Particulate Matter. In Industry 2, the average Pb concentration was also significantly higher than

Table 2 Summary of $PM_{2.5}$ and $PM_{2.5-10}$ average concentration (values in $ng\ m^{-3}$)

	Environment		Schools		Offices		Industry 1		Industry 2	
	$N = 104$		$N = 10$		$N = 4$		$N = 8$		$N = 8$	
	$PM_{2.5}$	$PM_{2.5-10}$	$PM_{2.5}$	$PM_{2.5-10}$	$PM_{2.5}$	$PM_{2.5-10}$	$PM_{2.5}$	$PM_{2.5-10}$	$PM_{2.5}$	$PM_{2.5-10}$
PM	24,000 ± 13,000	16,000 ± 9,400	9,100 ± 4,800	48,000 ± 28,000	11,000 ± 1,600	14,000 ± 1,600	420,000 ± 110,000	1,000,000 ± 520,000	60,000 ± 24,000	70,000 ± 76,000
Al	77 ± 110	180 ± 230	0.26 ± 0.10	0.80 ± 0.20	56 ± 7.8	140 ± 14	1,300 ± 170	3,100 ± 1,100	1,300 ± 930	920 ± 530
As	0.31 ± 0.32	0.16 ± 0.24	0.26 ± 0.10	0.80 ± 0.20	0.37 ± 0.12	0.17 ± 0.066	910 ± 420	1,300 ± 740	5.5 ± 3.1	0.6 ± 0.12
Br	3.0 ± 2.3	1.7 ± 2.0	0.26 ± 0.10	6.3 ± 1.8	1.0 ± 0.80	1.0 ± 0.80	330 ± 78	340 ± 220	1,900 ± 1,700	240 ± 220
Ca	230 ± 230	1,100 ± 900	4,700 ± 5,300	11,000 ± 5,000	400 ± 61	1,100 ± 260	940 ± 230	4,400 ± 1,300	560 ± 240	1,600 ± 700
Cl	160 ± 340	1,100 ± 1,100	0.14 ± 0.22	0.56 ± 0.35	53 ± 22	180 ± 99	19,000 ± 9,200	27,000 ± 15,000	400 ± 250	900 ± 570
Co	0.087 ± 0.070	0.12 ± 0.16	0.14 ± 0.22	0.56 ± 0.35						
Cr					3.0 ± 1.6	3.1 ± 1.1	230 ± 19	150 ± 210	27 ± 9.8	15 ± 5.0
Cu	5.4 ± 3.6	5.7 ± 4.3			22 ± 35	14 ± 20	300 ± 320	1,000 ± 1,200	28 ± 13	23 ± 7.6
Fe	120 ± 110	280 ± 340	140 ± 75	860 ± 420	64 ± 14	100 ± 47	2,500 ± 2,700	18,000 ± 20,000	270 ± 170	510 ± 260
Hg	0.13 ± 0.39	0.086 ± 0.075								
K	120 ± 95	150 ± 150	120 ± 48	1,100 ± 420	170 ± 13	130 ± 44	710 ± 300	1,100 ± 980	380 ± 490	170 ± 110
La	0.067 ± 0.048	0.17 ± 0.24	0.058 ± 0.061	0.76 ± 0.23						
Mn	2.3 ± 2.0	4.2 ± 4.9			1.9 ± 0.27	3.4 ± 1.2	51 ± 28	200 ± 150	14 ± 11	12 ± 4.7
Na	370 ± 350	1,100 ± 830	210 ± 110	1,500 ± 610	46 ± 7.3	75 ± 19	23,000 ± 4,100	110,000 ± 95,000	430 ± 140	1,000 ± 590
Ni	2.6 ± 1.6	1.6 ± 2.0			3.2 ± 0.66	1.6 ± 0.89	38 ± 21	190 ± 140	8.7 ± 3.5	11 ± 3.9
Pb	8.6 ± 8.5	6.0 ± 6.6			5.5 ± 1.0	5.3 ± 1.1	180,000 ± 91,000	340,000 ± 230,000	4,400 ± 4,300	15,000 ± 13,000
Si	200 ± 310	470 ± 620			150 ± 7.7	430 ± 97	610 ± 280	3,400 ± 890	750 ± 830	2,500 ± 1,900
S	850 ± 720	270 ± 200								
Sb	1.5 ± 1.5	1.1 ± 0.86	0.78 ± 0.58	3.9 ± 2.9	0.64 ± 0.14		33,000 ± 16,000	68,000 ± 84,000	52 ± 48	6.6 ± 4.1
Sc	0.013 ± 0.028	0.048 ± 0.093	0.023 ± 0.019	0.16 ± 0.11						
Se	3.7 ± 22	1.0 ± 4.1	0.73 ± 0.94	0.49 ± 0.18						
Sm	0.011 ± 0.017	0.031 ± 0.050	0.81 ± 1.9	0.14 ± 0.070						
Ti	8.5 ± 10	21 ± 27			5.1 ± 1.5	15 ± 4.3	150 ± 66	380 ± 320	23 ± 17	42 ± 16
V	6.7 ± 5.1	4.5 ± 6.0								
Zn	18 ± 20	18 ± 18	8.2 ± 3.6	86 ± 6.1	21 ± 9.0	40 ± 14	340 ± 160	920 ± 480	190 ± 180	210 ± 150
Cl ⁻	440 ± 490	1,400 ± 1,300								
NO ₃ ⁻	1,300 ± 1,100	1,000 ± 670								
SO ₄ ²⁻	3,900 ± 2,900	540 ± 280								
NH ₄ ⁺	1,300 ± 970	16 ± 21								
Ca ²⁺	380 ± 300	430 ± 170								
K ⁺	130 ± 130	43 ± 20								
Mg ²⁺	52 ± 34	110 ± 74								
Na ⁺	400 ± 300	990 ± 790								
H ⁺	4.2 ± 10									

in offices and in environment, being $4.4 \mu\text{g m}^{-3}$ for $PM_{2.5}$ and $15 \mu\text{g m}^{-3}$ for $PM_{2.5-10}$.

The most abundant species in the outdoor environment (concentrations generally higher than $1 \mu\text{g m}^{-3}$) in PM_{10} were SO_4^{2-} , NO_3^- , Cl^- , Na^+ , Ca and NH_4^+ . The SO_4^{2-} , NO_3^- and NH_4^+ were the largest components of $PM_{2.5}$, while Cl^- , Na^+ and Ca were abundant mainly in the coarse particle fraction. This fact was consistent with the expected contribution from anthropogenic sources for $PM_{2.5}$ and from marine aerosol and suspended dust for $PM_{2.5-10}$. Mainly in the summer, NO_3^- was also found abundantly in the coarse particle fraction, presumably due to the 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 [22].

Element concentrations measured in the offices and in the environment did not present significant differences. This fact was expected because offices have natural ventilation made by the open windows. Besides having also natural ventilation, the schools presented significant higher concentrations of Ca, Fe, K, La, Sc, Sm and Zn in $PM_{2.5-10}$ than in outdoor. The higher concentrations of Ca, Fe, K, La, Sc and Sm measured in the schools indicated that the most probable cause of increased classroom coarse particle concentrations was the penetration of mineral dust through the windows and the re-suspension of settled dust or suspension of soil material brought in by the children's shoes [6]. Ca was detected at very high concentrations ($11 \mu\text{g m}^{-3}$). This led to the idea that Ca could be attributed to a real indoor source, probably originating from the chalk (mainly CaSO_4), used in the blackboards, and/or the gypsum walls and plasters used as building materials. Inside the classrooms significant high concentrations of Zn were measured for the coarse fraction. This fact can be explained by the several products using Zn that are applied indoors to protect steel, walls, wood surfaces, doors and windows.

Particles composition as a function of size

The analysis of the granulometry of the particles has commonly been used as a first step in attempting to identify natural and anthropogenic sources of particles. INAA technique showed to be a very valuable technique to examine the particle composition as a function of particle size in the aerosols collected in the environment. Figure 1 shows that La, Sm, and Sc presented a very similar size distribution reflecting a common source emission which is the soil. They skewed to the larger size range and had one peak in the coarse particle region (2–4 and 4–8 μm). These two coarse fractions account for 62 % of La, 65 % of Sm, and 67 % of Sc concentration. Results for Na showed that 98 % of the mass were in particles between 2 and 8 μm in

agreement with a marine origin. As and Se presented the highest concentrations in the particles between 0.25 and $0.5 \mu\text{m}$ indicating the probable provenience of these compounds from anthropogenic activities [23].

Measuring APM for source apportionment

For the source apportionment which is a prerequisite for studying mitigation options in order to decrease the levels of APM—a multivariate data base containing key pollutant elements should be generated.

Therefore, the combination of multielement methods, such as INAA and PIXE, with specific statistical tools, including Principal Component Analysis (PCA) and Multilinear Regression Analysis (MLRA) are very suitable for such studies [22, 24, 25].

For the aerosols sampled in the outdoor environment, PCA applied to the fine particulate compounds identified seven main chemical profiles contributing to $PM_{2.5}$. The first factor represented the crustal contribution, given that it is defined by typical soil elements, such as Al, Si, Sc, Mn, Fe, La and Sm. The second factor was associated with fuel-oil combustion defined by Ni and V. The third factor represented the marine aerosol, as deduced from the high Na^+ , Cl^- and Mg^{2+} loading factors. The main components defining the fourth factor were SO_4^{2-} and NH_4^+ , which derived from gas to particle conversion processes of products of the SO_2 oxidation and NH_3 . The fifth factor was correlated with Zn, Cu and Sb, which were associated with coal combustion and traffic (mainly tires and brake wear rather than combustion processes). The chemical profile of the sixth factor was mainly defined by NO_3^- , which derives from gas to particle conversion processes of products of the NO_x oxidation, and it was expected to

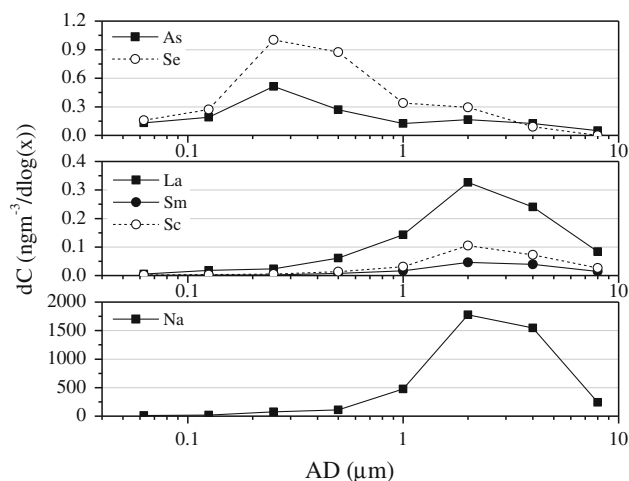


Fig. 1 As, Se, La, Sm, Sc and Na size distribution

provide mainly from vehicle exhaust. These sources accounted for 83 % of the total variance in the PCA.

For the $PM_{2.5-10}$, a similar source profile was identified. The major exception was the source correlated with NO_3^- , which was not identified, being this ion correlated with the secondary aerosol, in this size range. In the coarse fraction the identified sources account for 88 % of the total variance.

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 $PM_{2.5}$ and $PM_{2.5-10}$ total mass concentrations and as independent variables the principal component factor scores [22]. MLRA shows that in average, the largest contribution to $PM_{2.5}$ total mass was 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 presented seasonality, characterized by higher contributions of secondary aerosol (34 %), during spring or summer, due to the photo chemical reactions [26]; and higher vehicle exhaust (30 %) contributions during autumn or winter, associated with the preferential formation of ammonium nitrate at lower winter temperatures (Fig. 2).

In the coarse fraction, marine (47 %) and soil (20 %) contributions were predominant (Fig. 2). Secondary aerosol contribution decreased to 15 % in these coarse particles. Fuel oil combustion, Industry or traffic and Se/Hg emissions had an average contribution of 5, 13 and 0.4 %, respectively. Sea spray presented 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 was 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 [22].

Receptor modeling can profit from its capability to discriminate sources based on relative variations in concentrations if the strengths of the different sources vary differently in time. In most urban regions road traffic and industrial activities vary substantially between weekdays and Sundays, with a strong decrease on the weekend [27]. The source contributions calculated by PCA/MLRA for weekdays and Sundays was used to further differentiate the contribution of road vehicles, to the aerosol load in the studied Lisbon industrial-urban area [28].

The larger differences between weekdays/weekends occurred during autumn/winter periods for soil dust. The levels of soil dust were on average two (in coarse particles) to three (in fine particles) times higher, in working days, during colder months. Soil dust was associated with the

road traffic activity as result of re-suspended particles from road dust. Much weaker variability between working days and Sundays during spring/summer periods, although there was also a tendency for higher source contributions during working days, principally for the dust-related source. The lower impact of decreasing weekend anthropogenic activities during warmer months was presumably related with better dispersion conditions during this period of the year, associated with higher source emission of natural dust by the action of the wind, which is favoured by the warmer and drier weather. In summer, there was possibly a more important input from regional sources that weakens the effect of the weekend local source variability. Presumably, in colder months, there was a higher contribution of local and urban sources to the aerosol load.

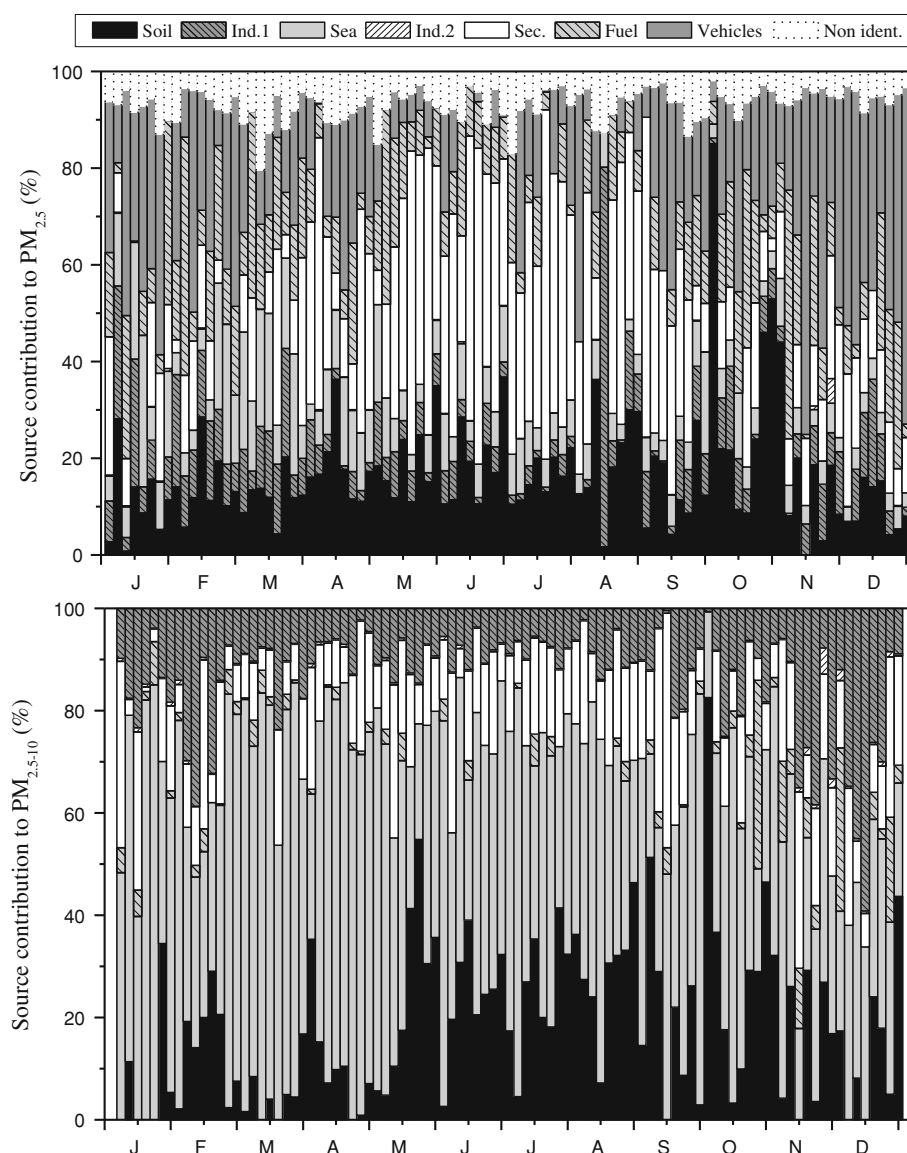
Measuring APM for the identification of long range transport

It has long been recognized that Saharan dust may be transported a long way from its sources, particularly over the ocean and especially over the North Atlantic and over various areas of the Mediterranean. Sahara desert is responsible for the global emission of 50 % of the total mass of mineral aerosols to the atmosphere. APM from this source region consists mainly of clay minerals, Ca and Mg carbonates, with minor proportions of sulphate, nitrate and carbonaceous particles. These chemical features clearly contrast with the urban anthropogenic particles. The impact of the long range transport of North African dust on PM_{10} levels recorded in air quality monitoring stations in Lisbon has been demonstrated [29]. It is important to identify these events because the European Union PM_{10} limit values are frequently exceeded due to long range transport and not due to local sources.

Some NATs, such as PIXE and INAA, can be used in order to give an insight on the APM provenance of the aerosols because they allow an accurate and precise determination of some mineral elements such as Al, Fe, La, Sc, Si and Sm [30].

Figure 3a shows that PM_{10} , Al, Si and Fe time series do not present a clear structure in the seasonal variations. Several high concentrations episodes could be seen simultaneously for the PM_{10} and for the three elements. The highest peak was registered in 11th October. Hysplit Model, ending in Bobadela in 11th October, confirmed an air mass transport from North of Africa (Fig. 3b). In the studied industrial-urban area, this Sahara transport event resulted in concentration peaks for Al, Fe and Si of 2,600, 4,100 and 7,900 $ng.m^{-3}$, respectively (when 2001 annual average concentration were 260, 400 and 660 $ng.m^{-3}$, respectively).

Fig. 2 Relative source contribution for $PM_{2.5}$ and $PM_{2.5-10}$ total mass concentration



Integrating the element analysis of APM and human biomonitoring for occupational health assessment

A key issue for risk assessment in occupational health is the characterization of dose at the target organ level. In the case of inhalable pneumotoxic metals a noninvasive method for sampling from the lung would be extremely useful. In the last years, an effort has been made to identify, in the Exhaled Breath Condensate (EBC) air, bioindicators of respiratory system pathologies and response to toxic substances. However, the elemental characterization of the EBC for environmental health purposes is still in its infancy with lots of questions remaining unanswered. The objective of this work was to investigate whether EBC can be used for a better risk assessment among human exposure

to heavy metals. For that, EBC was collected in three groups of volunteers working in: offices (control group), Industry 1 and 2 and element concentrations were measured by TXRF and ICP-MS [15]. Table 2 shows that these three groups were exposed to different concentration of metals during their working activities.

Figure 4 presents the mean Cr, Ni, Cu, Sb, and Pb concentrations measured in the EBC of workers from Industry 1 and 2 and of non-exposed individuals. EBC results showed a significant difference between workers and non-exposed individuals for all elements. Elemental concentrations from Industry 1 workers were significantly higher than from Industry 2, reflecting the influence of exposure to high levels of these pollutants according to the measured APM elemental concentrations (see Table 2).

Fig. 3 a Time series for PM_{10} , Al, Si and Fe concentrations from January 2001 to December 2001 (values in $ng\ m^{-3}$), **b** backward trajectories ending in Bobadela at 11th October 2001, calculated with Hysplit Model from NOAA

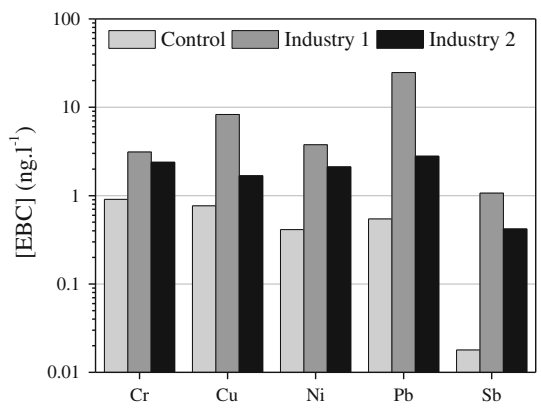
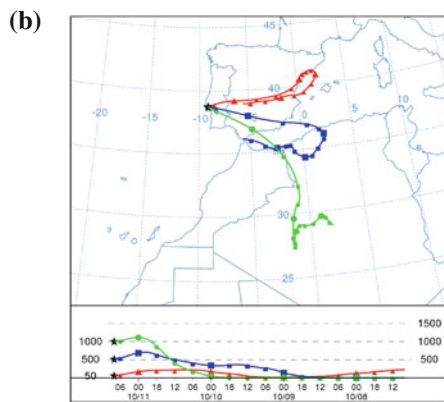
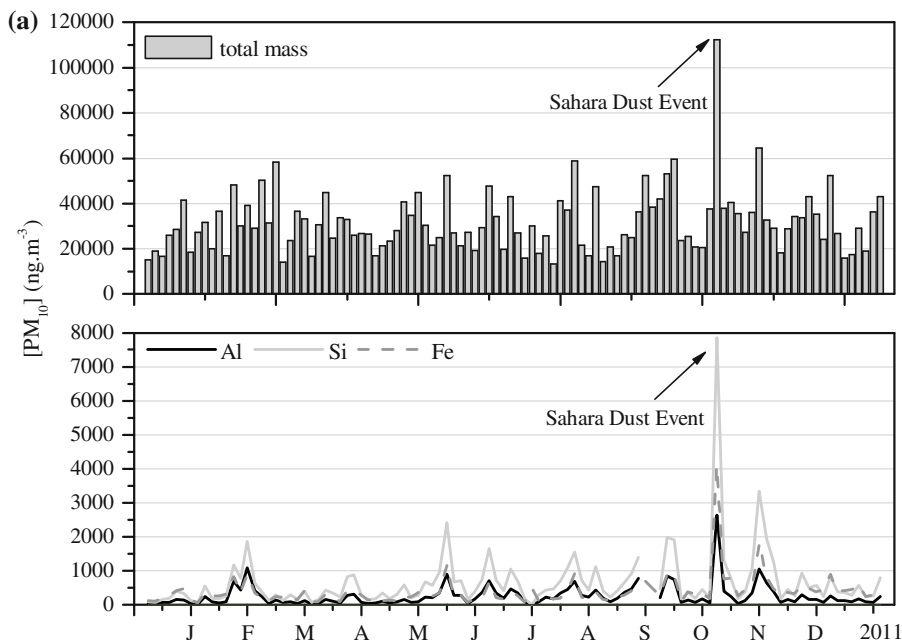


Fig. 4 Mean concentration values ($ng\ l^{-1}$) of elements measured in the EBC sampled in workers from both Industry 1 and 2 and in non-exposed group

These results may suggest that EBC method could be regarded as a viable tool for occupational exposure assessment.

Conclusions

The NATs multielement capability in association with low detection limits makes possible the determination of elements that are important due to their toxicity or due to their association to specific sources. The achievements presented in this paper related to 1) the element composition of APM sampled in different environments, 2) the particle size distribution, 3) the source apportionment, 4) the identification of long range transport and 5) the health assessment, confirm the relevance of NATs as efficient analytical techniques in such studies.

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