

Approaching $PM_{2.5}$ and $PM_{2.5-10}$ source apportionment by mass balance analysis, principal component analysis and particle size distribution

S.M. Almeida^{a,b,*}, C.A. Pio^b, M.C. Freitas^a, M.A. Reis^a, M.A. Trancoso^c

^a Instituto Tecnológico e Nuclear, EN10, apartado 21, 2683-953 Sacavém, Portugal

^b Universidade de Aveiro, DAO, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal

^c Instituto Nacional de Engenharia, Tecnologia e Inovação, LAACQ, Estrada do Paço do Lumiar 22, 1649-038 Lisboa, Portugal

Received 18 July 2005; received in revised form 2 March 2006; accepted 21 March 2006

Available online 24 May 2006

Abstract

A chemical characterization was carried out for $PM_{2.5}$ and $PM_{2.5-10}$ samples collected in a suburban area and the concentrations of 12 elements were determined in 8 size segregated fractions using a Berner Impactor. Two main objectives were proposed in this work: 1) to test for closure among chemical and gravimetric measurements of $PM_{2.5}$ and $PM_{2.5-10}$ and 2) evaluate the performance of Multilinear Regression Analysis (MLRA) and Mass Balance Analysis (MBA) in the determination of source contribution to Particulate Matter (PM) concentrations. The fraction unaccounted for by chemical analysis comprised on average 17% and 34% of gravimetric $PM_{2.5}$ and $PM_{2.5-10}$, respectively. The lack of closure in $PM_{2.5}$ and $PM_{2.5-10}$ mass (i.e., constituent concentrations not adding up to gravimetrically measured) could partly result from the presence of water associated with particles and errors in the estimation of unmeasured species. MLRA and MBA showed very similar results for the temporal variation of the source contributions. However, quantitatively important discrepancies could be observed, principally due to the lack of mass closure in $PM_{2.5}$ and $PM_{2.5-10}$. Both methods indicated that the major $PM_{2.5}$ aerosol mass contributors included secondary aerosol and vehicle exhaust. In the coarse fraction, marine and mineral aerosol contributions were predominant.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Fine particles; Coarse particles; Mass closure; Multilinear regression analysis; Berner Impactor

1. Introduction

Epidemiological studies have consistently shown an association between PM pollution and the number of deaths from cancer and cardiovascular and respiratory

diseases (Pope et al., 2002). There is also evidence linking particulate air pollution and increases in hospital admissions for respiratory (Roemer et al., 1993; Pope, 1991; Burnett et al., 1995) and cardiovascular diseases (Burnett et al., 1995; Schwartz and Morris, 1995). Epidemiological studies show that atmospheric fine particles ($PM_{2.5}$) are specifically responsible for these associations (Pope et al., 2002; Schwartz et al., 1996; Dockery et al., 1993).

In order to evaluate and to reduce the impact of aerosols on health, any program aimed at controlling the

* Corresponding author. Instituto Tecnológico e Nuclear, EN10, apartado 21, 2683-953 Sacavém, Portugal. Tel.: +351 219946153; fax: +351 219941039.

E-mail address: smarta@itn.pt (S.M. Almeida).

levels of PM demands the knowledge of the particles size distribution, chemical composition and sources.

Over the years efforts have been made to get knowledge about the composition of atmospheric aerosols as a function of size (Almeida et al., 2005; Putaud et al., 2004) and to achieve mass closure on the chemical species for the whole mass of aerosol collected (Tsyro, 2005; Chan et al., 1997; Harrison et al., 2003; Andrews et al., 2000). Analytical chemistry has been used to measure a large proportion of the periodic table elements, in the aerosol, attempting to gain knowledge as complete as possible about the chemical composition and emission sources. However, despite very extensive chemical analyses, mass closure is rarely achieved. Even if the important aerosols components (inorganic and carbonaceous compounds, minerals and metals) are analysed, a fraction of PM mass remains unidentified (Tsyro, 2005; Chan et al., 1997; Harrison et al., 2003; Andrews et al., 2000). Moreover, the use of the mass balance approach in the identification of sources and in the estimation of their contribution is too time consuming and expensive to be applicable in a routine basis.

An alternative to examine the contribution of sources is to use Receptor Models. Some success has been achieved in the apportionment of both particle mass and specific airborne particles components to specific source categories using models based on multivariate statistics (Almeida et al., 2005; Chan et al., 1999; Pio et al., 1996; Rodríguez et al., 2002). With such models, the study can be deliberately restricted to a smaller number of components, which can be used as tracers of sources. These tracers can represent unmeasured compounds, providing a simple but effective analysis. Therefore, realistic information about the contribution of the sources can be extracted, avoiding the trends associated with mass closure and with approximations to infer elements, such as oxygen and hydrogen, which are usually not chemically analysed.

2. Experimental

2.1. Description of the sampling equipment

In a suburban area located at the outskirts of Lisbon, PM was collected during 24 h periods with one low volume and one high volume sampler, which operated side by side.

The low volume Gent sampler was equipped with a PM₁₀ pre-impactor stage and a Stacked Filter Unit (SFU) which carried, in two different stages, two 47 mm Nuclepore polycarbonate filters, with 8 and 0.4 µm pore size. 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 (Maenhaut, 1992).

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

PM was also collected with a Berner Impactor (Hauke LPI 30/0,06/2) in four periods (Autumn, Winter, Spring and Summer) of 72 h each. The device used 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.

2.2. Gravimetric and chemical analysis

Nuclepore and Quartz fibre filters were weighed before and after sampling at a 50% relative humidity.

Some discrepancies were observed in the total mass concentration obtained by the High-vol sampler and by the Gent sampler attributed to cut-point differences of the individual samplers, differences in filters collection and accuracy and precision of weightings (regression analysis of High-Vol concentrations vs. Gent concentrations presented a correlation of 0.72 for PM_{2.5} and 0.87 for PM_{2.5–10}, more details in Almeida, 2004). For subsequent calculations only the total mass concentration obtained by the Hi-Vol sampler was considered. Therefore, the concentration of species sampled with the Gent collector was normalized, by comparison to the high volume total mass concentration; for that Eq. (1) was employed:

$$[X]_{\text{normalized}} = \frac{[X]}{[PM_{\text{total}}]_{\text{Gent}}} \times [PM_{\text{total}}]_{\text{Hi-vol}} \quad (1)$$

Samples collected in Nuclepore filters (Gent sampler) were used for elemental analysis. The exposed filters were cut into three parts: half was analyzed by an Instrumental Neutron Activation Analysis (INAA) (Bowen and Gibbons, 1963) with the *k₀* methodology (De Corte, 1987); a quarter was analyzed by a Particle Induced X-Ray Emission (PIXE) (Johansson and Campbell, 1988); and the other quarter was kept in storage for other possible measurements or replicates. The complementary nature of the two techniques

allowed the determination of Al, Br, Cu, K, Mn, Ni, Pb, Si, Ti, V and Zn by PIXE and As, Co, Fe, Hg, La, Sb, Sc, Se and Sm by INAA. Nuclepore filters provided by the Berner Impactor were analysed by INAA to determine As, Co, Fe, Hg, K, La, Na, Sb, Sc, Se, Sm and Zn.

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

Exposed Quartz fibre filters were used for the determination of water soluble inorganic ions and for measurement of Black Carbon (BC) and Organic Carbon (OC) content. For water soluble ions determination, one portion of the filter was extracted with distilled deionised water by ultrasonic and mechanical shaking and filtered through a pre-washed Whatman 42 filter. The aqueous extract was analyzed by Ion Chromatography (Chow and Watson, 1999) (Cl^- , NO_3^- and SO_4^{2-}), Indophenol-blue Spectrophotometry (Weatherburn, 1967) (NH_4^+) and Atomic Absorption/Emission Spectroscopy (Grohse, 1999) (Ca^+ , Mg^{2+} , Na^+ and K^+).

BC and OC contents were determined in another portion of the Quartz fibre filter with a thermo-optical system, based on the thermal desorption/oxidation to CO_2 with subsequent determination by non-dispersive infrared spectrophotometry (Pio et al., 1993).

2.3. PCA, MLRA and BQM procedures

Source categories for $\text{PM}_{2.5}$ and $\text{PM}_{2.5-10}$ constituents were identified by means of Principal Component Factor Analysis (PCA) using a STATISTICA software. This was performed by using 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.

The contribution of each source group to the aerosol burden was then quantitatively assessed by means of a Multi Linear Regression Analysis (MLRA). MLRA was applied to the experimental data, using $\text{PM}_{2.5}$ and $\text{PM}_{2.5-10}$ concentrations as dependent variables; the independent variables were the principal component

Table 1

Method used to calculate the source contribution based on Mass Balance Analysis (OC—organic carbon; BC — black carbon)

	$\text{PM}_{2.5}$	$\text{PM}_{2.5-10}$
Soil	1.89Al+2.14Si+1.4Ca+ 1.43Fe+1.71Sc+1.67Ti+ 1.41Co+1.39Mn+ 1.17La+1.16Sm	1.89Al+2.14Si+1.4Ca+ 1.43Fe+1.71Sc+1.67Ti+ 1.39Mn+1.41Co+ 1.17La+1.16Sm + (K-K ⁺)
Sea	Na ⁺ +Cl ⁻ +Mg ²⁺ +Br+ SO ₄ ²⁻ _m	Na ⁺ +Cl ⁻ +Mg ²⁺ + SO ₄ ²⁻ _m +K ⁺
Secondary aerosol	SO ₄ ²⁻ _{nm} +NH ₄ ⁺	SO ₄ ²⁻ _{nm} +NH ₄ ⁺ +NO ₃ ⁻
Fuel combustion	V+Ni+Pb	V+Ni+As+Br+Pb
Industry/traffic	Cu+Zn+Sb	Cu+Zn+Sb+1.6OC+BC
Se/Hg	Se+Hg	Se+Hg
Vehicle exhaust	NO ₃ ⁻ +As+K+1.6OC+ BC	

factor scores, calculated by introducing a fictitious sample with null concentrations for all variables (Thurston and Spengler, 1985). Details of source apportionment methodology and results are presented in Almeida (2004) and Almeida et al. (2005).

The second method employed for calculating the source contribution is based on Mass Balance Analysis (MBA) of the species associated with each principal component. The contribution of each source was estimated as the sum of the PM species associated with each PCA principal component. The PM species associated with several principal components were added to the component with higher factor loading. In MBA some approximations were made to infer some unmeasured chemical species. Details are presented in Table 1.

Results provided by the two methodologies (PCA/MLRA and MBA) were compared and discussed.

3. Results

The fine particulate mass concentration varied between 2.4 and 30 $\mu\text{g m}^{-3}$ and had a mean value of 14 $\mu\text{g m}^{-3}$. The coarse particulate mass concentration varied between 4 and 88 $\mu\text{g m}^{-3}$ and had a mean value of 18 $\mu\text{g m}^{-3}$. PM_{10} average concentrations were above the EU annual PM_{10} standard of 20 $\mu\text{g m}^{-3}$ targeted for 2010. The EU 24 h PM_{10} limit value of 50 $\mu\text{g m}^{-3}$ was exceeded more than 7 times in the three years of study. The scenario may be worst because only 104 days per year were analysed in Bobadela.

The most abundant species (concentrations generally higher than 1 $\mu\text{g m}^{-3}$) in particulate matter were OC, SO_4^{2-} , NO_3^- , Cl^- , BC, Na^+ , total Ca and NH_4^+ . Species with an anthropogenic origin, such as OC, SO_4^{2-} ,

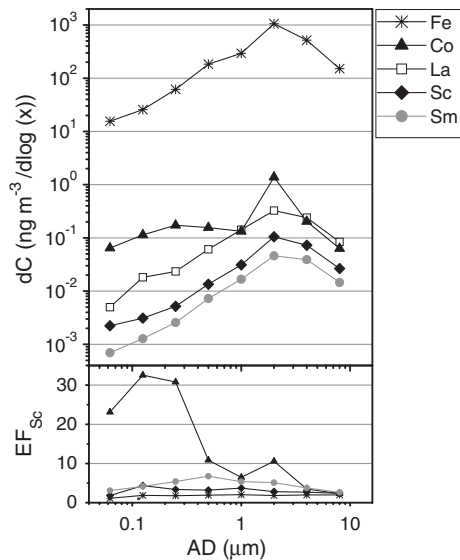


Fig. 1. Fe, Co, La, Sc and Sm size distribution and enrichment factor, using Sc as a reference element (EF_{Sc}).

NO_3^- , BC and NH_4^+ , present concentrations comparable with other urban European cities (Van Dingenen et al., 2004). In South European regions, such as Portugal, in addition to anthropogenic sources, the ambient aerosol has an important contribution from natural dust, due to local emissions from bare soil, and an influence of episodic African dust transport outbreaks (Almeida et al., 2005; Rodríguez et al., 2002). Concentrations of mineral elements, measured in this work, reflected this phenomenon. Moreover, high concentrations of sea salt species were registered in Lisbon because the Portuguese coastal areas have an important input of marine aerosol (Pio et al., 1996; Almeida et al., 2005).

3.1. Reconstruction of chemical composition in aerosols

It was assumed that aerosols can be classified into eight types: crustal matter, sea salt, ammonium, sulphate, nitrate, organic matter, black carbon and minor elements. The study of the particle size distribution, using the Berner Impactor, allowed the association of particle species with a similar pattern, which suggested a common origin.

3.1.1. Crustal matter

To examine the particle composition and sources as a function of particle size, the elemental concentration was averaged over all four samples for each Berner Impactor stage. Results presented very similar size distribution for La, Sm, Fe and Sc (Fig. 1). 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, 67% of Fe and 67% of Sc concentration. The crustal enrichment factor method was used as an attempt to evaluate the strength of the crustal and non-crustal origin. Enrichment factors, using Sc as a crustal reference element (EF_{Sc}) were calculated using Mason and Moore (1982) soil composition. La, Sm, Fe and Sc EF_{Sc} varied relatively little as a function of particle size. These elements presented EF_{Sc} lower than 10 in all stages, suggesting strong mineral contribution. Co presented higher EF_{Sc} in the finest fraction (between 0.0625 and 0.5) suggesting the association to other source.

Al, Si and Mn presented EF_{Sc} lower than 10 for $PM_{2.5}$ and $PM_{2.5-10}$ fractions suggesting a mineral provenance.

Based on these results, the crustal matter concentration was estimated by summing the concentrations of Al, Si, Fe, Sc, Ti, Mn, Co, Ca, La and Sm, assuming that these elements are present in soil as oxides.

In coarse fraction, insoluble potassium (obtained from the difference between total potassium and water soluble potassium) was included in the crustal source. Berner results for K (Fig. 2), showed that the mass size distribution is represented as a bimodal distribution having two peaks in the stages 0.25–0.5 and 2–4 μm . EF_{Sc} for K presented enrichment for particles with AD lower than 0.5 μm , suggesting a non mineral origin,

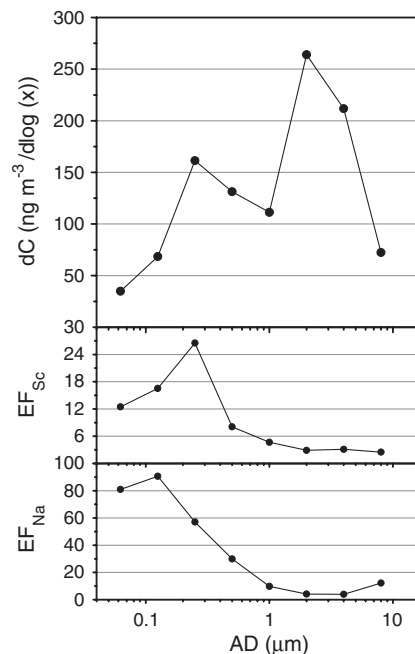


Fig. 2. Potassium size distribution and enrichment factors, using Sc (EF_{Sc}) and Na (EF_{Na}) as reference elements.

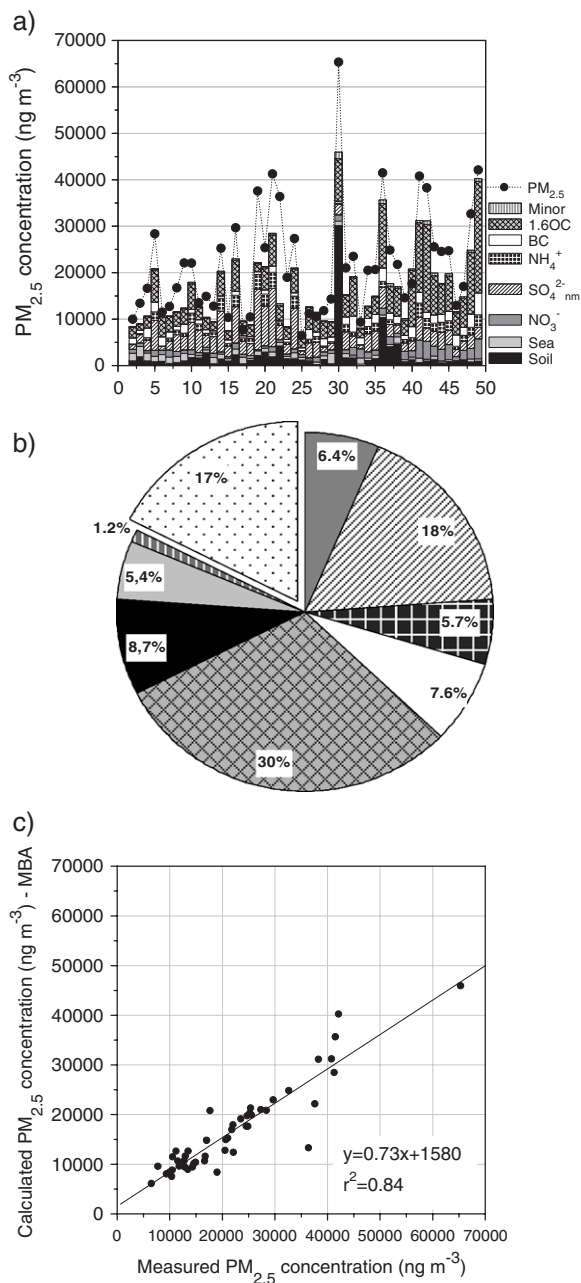


Fig. 3. a) Daily contribution to $PM_{2.5}$ of soil, sea, NO_3^- , SO_4^{2-} , NH_4^+ , black carbon (BC), organic matter (1.6OC) and minor species. $PM_{2.5}$ mass concentration measured by gravimetry. b) Average contribution to $PM_{2.5}$ of soil, sea, NO_3^- , SO_4^{2-} , NH_4^+ , black carbon (BC), organic matter (1.6OC) and minor species. c) Relation between $PM_{2.5}$ concentration calculated by MBA and determined by gravimetry.

probably associated with biomass burning. A marine enrichment factor was calculated as an attempt to evaluate the strength of the sea salt origin. Enrichment factors, using Na as a marine reference element (EF_{Na})

were calculated using Bowen (1979) sea water composition. Results showed EF_{Na} lower than 10 for particles with AD between 1 and 8 μm , indicating a marine influence on these particle sizes. Previous studies (Almeida, 2004; Almeida et al., 2005) revealed that insoluble coarse potassium had a geological origin, whereas soluble potassium had a marine provenance.

Figs. 3b and 4b show that the mineral aerosol contributed on average for 19% of coarse particles and 8.7% of fine particles masses. The highest mineral contribution observed in both fine and coarse fractions were reached during a South Continental air mass transport and occurred on 11th October 2001. On that date the mineral aerosol contributed to 30% of coarse particles and 46% of fine particles mass. This event resulted in PM_{10} concentration peaks for Al, Si, Ca and Fe of 2630, 7860, 6450 and 4080 ng m⁻³, respectively. This is due to an important contribution of long range transported soil emissions, namely from the interior of the Iberian Peninsula and the Saharan desert (Almeida et al., 2005). This transport of dust could explain the low difference of mineral loads for the fine and coarse fractions. Finer particles have higher residence times and can undergo long range transport. Figs. 3a and 4a show

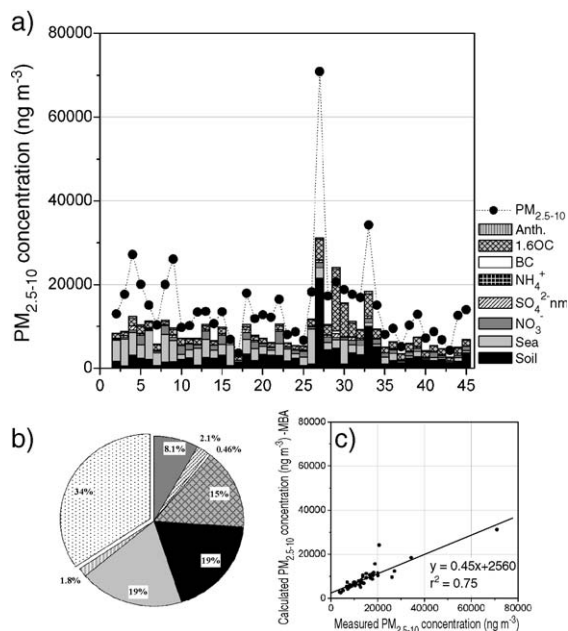


Fig. 4. a) Daily contribution to $PM_{2.5-10}$ of soil, sea, NO_3^- , SO_4^{2-} , NH_4^+ , black carbon (BC), organic matter (1.6OC) and minor species. $PM_{2.5-10}$ mass concentration measured by gravimetry. b) Average contribution to $PM_{2.5-10}$ of soil, sea, NO_3^- , SO_4^{2-} , NH_4^+ , black carbon (BC), organic matter (1.6OC) and minor species. c) Relation between $PM_{2.5-10}$ concentration calculated by MBA and determined by gravimetry.

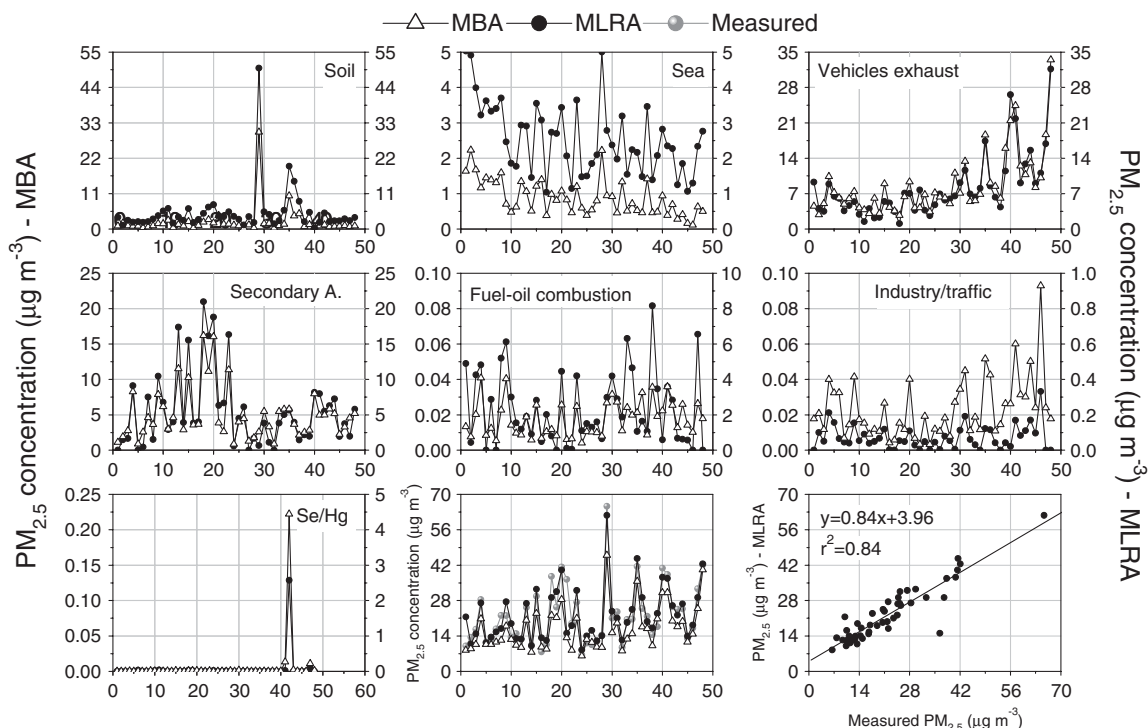


Fig. 5. Daily sources contribution to $PM_{2.5}$ obtained by MBA and MLRA. Comparison between $PM_{2.5}$ total mass concentration determined by MBA and MLRA and measured by gravimetry. Relation between $PM_{2.5}$ concentration calculated by MLRA and determined by gravimetry.

that the effect of Sahara dust transport in 11th October was higher in the fine fraction.

Soil contribution was also determined by PCA/MLRA. The estimated crustal contributions using this method and using MBA were highly correlated ($r^2=0.96$ for $PM_{2.5}$ and $r^2=0.89$ for $PM_{2.5-10}$) (Figs. 5 and 6). PCA/MLRA estimated a soil contribution of 20% for $PM_{2.5-10}$ and 16% for $PM_{2.5}$ (Table 2). Results obtained for $PM_{2.5-10}$ were very similar; however, the soil contribution for $PM_{2.5}$ calculated using PCA/MLRA was approximately a factor of 2 larger than the contribution calculated using MBA. The lower MBA results are not surprising because this technique did not include all compounds known to contribute to dust and assumed that these elements are only present as oxides. According to Andrews et al. (2000) the mass estimated using the sum of the oxides could be lower than the actual soil mass up to 50%. Moreover, some dust species are hygroscopic and some water might be associated with dust, which was not taken into account by MBA.

3.1.2. Sea salt

The marine contribution was calculated as the sum of Na^+ , Cl^- , Mg^{2+} and of a fraction of the total sulphate

(marine sulphate). Concentrations of marine sulphate were calculated based on Eqs. (2) and (3), which assumed that 1) the chemical composition of sea salt particles was the same as that of sea water and 2) Na^+ in particulate samples originated solely from sea salt. The Berner Impactor results showed that 98% of the Na mass were in particles between 2 and 8 μm in agreement with a marine origin.

$$[SO_{4\ m}^{2-}] = [SO_4^{2-}] - [SO_{4\ nm}^{2-}] \quad (2)$$

$$[SO_{4\ nm}^{2-}] = [SO_4^{2-}] - [Na^+] \times \left(\frac{[SO_4^{2-}]}{[Na^+]} \right)_{\text{sea.water}} \quad (3)$$

In the coarse fraction, soluble potassium was also included as a marine contribution.

Sea spray represented respectively, 19% and 5.4% of $PM_{2.5-10}$ and $PM_{2.5}$ mass loading. The highest concentrations of marine ions, observed in Fig. 4a, were reached during Maritime air mass transport (Almeida, 2004). Portuguese coastal areas have an important input of marine aerosol, due to the geographic position of Portugal (at the extreme southwest of Europe) and the dominant western wind regime. The latter originates by

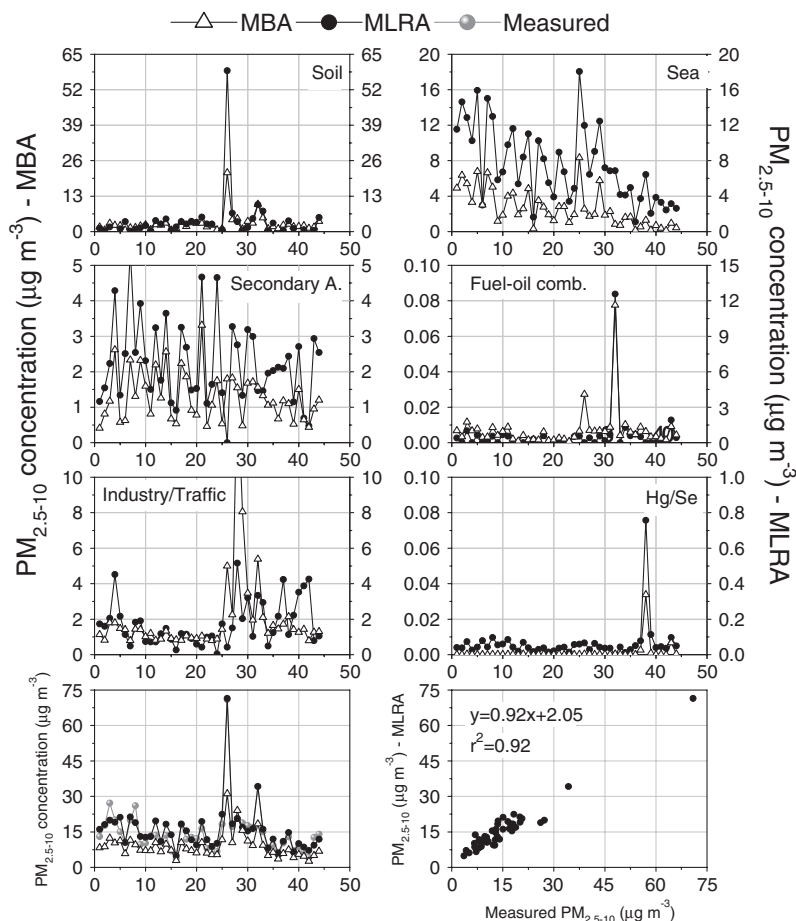


Fig. 6. Daily sources contribution to $PM_{2.5-10}$ obtained by MBA and MLRA. Comparison between $PM_{2.5-10}$ total mass concentration determined by MBA and MLRA and measured by gravimetry. Relation between $PM_{2.5-10}$ concentration calculated by MLRA and determined by gravimetry.

the presence of the semi-permanent Azores high-pressure and the Icelandic low-pressure systems over the North Atlantic Ocean.

The calculated marine contributions using the MBA and PCA/MLRA are highly correlated ($r^2=0.87$ for $PM_{2.5}$ and $r^2=0.88$ for $PM_{2.5-10}$) (Figs. 5 and 6). The PCA/MLRA estimated a marine contribution of 47% for $PM_{2.5-10}$ and 8% for $PM_{2.5}$ (Table 2). In the coarse fraction, there is a larger discrepancy of the results obtained by the two methods. Probably MBA does not include all components associated with sea water spray. Moreover, the principal species associated with this component— Na^+ , Mg^{2+} , and Cl^- are very polar and water soluble. Therefore, it is possible that part of the water adsorbed and/or absorbed in the particles was associated with these ions and, consequently, included in this component by the MLRA.

In addition, several studies (Pio and Lopes, 1998, Almeida et al., 2005) have shown that there is

usually a deficit of Cl^- with respect to the marine Na^+/Cl^- ratio in sea salt originated aerosol. The deficit has been suggested to be the result of the reaction of $NaCl$ with acidic species (HNO_3 , SO_2 and H_2SO_4) leading to a displacement of Cl^- as HCl (Pio and Lopes, 1998). The percentage of chloride lost from sea salt particles decreases with increasing particle size, because smaller particles have higher surface-to-volume ratio and longer atmospheric residence time (Harrison and Pio, 1983). However, due to the higher Cl^- concentration in coarse fraction, the absolute amount of volatilized Cl^- may be higher in this size range. Therefore, despite being emitted by the sea, Cl^- is not fully present in particulate form at the receptor and consequently, it was not considered in MBA. However, it is possible that the PCA/MLRA considered the total contribution of the sea, associating to this source the acidic compounds that displace Cl from sea salt.

Table 2
Mean source contribution to PM_{2.5} and PM_{2.5–10} obtained by MLRA and MBA methods

	PM _{2.5}		PM _{2.5–10}	
	MLRA	MBA	MLRA	MBA
Soil	16%	8.7%	20%	19%
Sea	8%	5.3%	47%	19%
Secondary aerosol	25%	23%	15%	10%
Fuel combustion	8%	0.087%	5%	0.045%
Industry/traffic	14%	0.12%	13%	16%
Se/Hg	0.2%	0.023%	0.4%	0.0091%
Vehicle exhaust	22%	45%	–	–
Non identified	6.8%	18%	0%	36%

3.1.3. Ammonium, sulphate, nitrate, organic carbon and black carbon

SO₄²⁻_{nm}, NH₄⁺, NO₃⁻, organic carbon and black carbon are the major components of the aerosols; consequently, they were considered separately.

In the fine fraction, SO₄²⁻_{nm} is one of the major secondary components of airborne particles, being highly neutralized by ammonia. In summer, SO₄²⁻_{nm} and NH₄⁺ concentrations presented a strong correlation ($r^2=0.92$, slope=1.2, in equivalents.m⁻³), which indicates that SO₄²⁻_{nm} was mainly present as (NH₄)₂SO₄ and/or NH₄HSO₄. In winter, ammonium was in excess, in relation to sulphate, and associates to other anions, mainly fine nitrates. In winter, regression analysis of NO₃⁻ vs. NH₄⁺ resulted in $r^2=0.83$ and slope=0.4. This might be due to the strong solar radiation in summer, which increases both temperature and the formation of OH radicals, promoting 1) the formation of secondary sulphates, which are transported at longer distances than the gaseous precursors and 2) the evaporation of ammonium nitrate. Consequently, SO₄²⁻_{nm} in the fine particles accounted for 24% in summer and 11% in winter.

In the warm season, the occurrence of NO₃⁻ was mainly attributed to the reaction of gaseous HNO₃ with mineral species such as calcium carbonate and with sea salt to form coarse Ca(NO₃)₂ and NaNO₃, respectively. The latter is strongly supported by the Na/Cl excess observed in warm seasons (Almeida et al., 2005), given that the reactions leading to NaNO₃ formation induced Cl volatilization. The NO₃⁻ mass represented 6.4% and 8.1% of the total mass for fine and coarse fraction, respectively.

The chemical composition of the organic fraction of aerosol was unknown and was estimated by multiplying the measured concentration of organic carbon by a conversion factor. In the literature, this factor ranges between 1.2 and 1.6 (Seinfeld and Pandis, 1998),

although some authors (Turpin and Lim, 2001) estimate higher values, going up to values above 2. During the CARBOSOL campaign elemental analysis was performed for the water soluble organic carbon (WSOC) mass fraction and showed values going from 1.7 in winter to 1.9 in summer (Duarte et al., submitted for publication). Taking into account that the average ratio of WSOC/OC is 56% it is not expected that the multiplying factor to transform OC carbon into OC mass will be higher than 1.6. Therefore, in the present work, this value was adopted through all calculations. Organic matter was the major component of PM_{2.5}, accounting for 30% of the total mass.

Black carbon arises from burning of carbonaceous fuels, in urban areas predominantly from road traffic. In PM_{2.5}, black carbon accounted for 7.6% of the total mass.

PCA identified one component, associated with the secondary aerosols, defined by SO₄²⁻ and NH₄⁺ in PM_{2.5} and by SO₄²⁻, NH₄⁺ and NO₃⁻ in PM_{2.5–10}. To compare the PCA/MLRA and MBA results, in fine fraction, SO₄²⁻ and NH₄⁺ were added. In the coarse fraction, NO₃⁻ was also added to this component (Table 1). Results showed that the two methods estimated a similar secondary aerosol contribution for the fine fraction (25%—MLRA and 23%—MBA) and for coarse fraction (15%—MLRA and 10%—MBA) (Table 2).

In the fine fraction, PCA identified a source defined by NO₃⁻, organic carbon, black carbon, As and K, which is expected to provide from vehicles exhaust (Almeida, 2004). The MBA summed these species and obtained a contribution of 41%, a factor of approximately 2 larger than the contribution calculated using the PCA/MLRA (22%) (Table 2), although highly correlated ($r^2=0.88$). This happened possibly because MBA included all NO₃⁻, organic carbon, black carbon, As and K masses in this component. However, NO₃⁻ was also associated with secondary aerosols component; organic carbon could originate from secondary gas to particle conversion; As could be emitted by coal combustion; and K could result from biomass burn. This led to overestimation of concentration in vehicle exhaust and to underestimation in other components, as can be observed in Table 2 for fuel combustion, industry/traffic and Se/Hg contributions.

3.1.4. Trace elements

Minor aerosol components—V, Ni, Cu, Zn, As, Se, Br, Sb, Hg and K (only in the fine fraction) were summed in a component and added to the analysis. The Berner Impactor results for Zn, As, Se, Sb and Hg are presented in Fig. 7. The mass size distribution for these

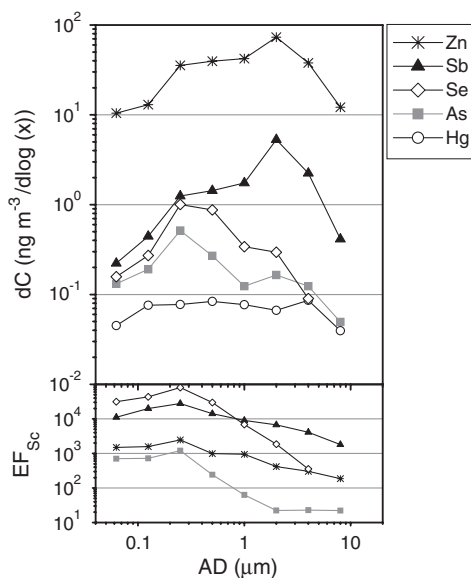


Fig. 7. Zn, Sb, Se, As and Hg size distribution and enrichment factor, using Sc as a reference element (EF_{Sc}).

elements did not present a common similar pattern. However, very high EF_{Sc} could be observed for all of them, suggesting an anthropogenic origin. In coarse fractions, these elements presented lower EF_{Sc} , probably associated with a soil or dust resuspension origin. Se and As, usually associated with coal combustion, skewed to the smaller size range and had only one peak in the fine fraction region. Zn and Sb not only had similar mass size distributions with a peak in the fraction 2–4 μm , but also similar EF_{Sc} patterns. This fact could indicate the existence of a common source. These elements are usually associated with various different sources nominally coal combustion, incineration and traffic (mainly tires and brake wear, rather than combustion processes) (Sternbeck et al., 2002).

This factor only represented 1.2% of the $PM_{2.5}$ total mass and 1.8% of the $PM_{2.5-10}$ total mass. However, these elements were also added to the analysis, because they have a great environment importance, due to their toxicity and anthropogenic origin.

3.1.5. Mass closure

$PM_{2.5}$ and $PM_{2.5-10}$ results were subjected to a mass closure test to determine whether the measurement of gravimetric fine and coarse PM concentration of a sample is equal to the sum of the concentrations of the individually identified species. This test was used to check data consistency, to characterize the relative contribution of the different components to PM, and to reassess the plausibility of common assumptions used

in the literature for estimating particle composition from chemical measurements. If closure is not achieved, the instruments, methods and assumptions used demand evaluation to identify areas which need further study.

On average, the total mass of the measured and estimated species by MBA explained, respectively, 83% and 66% of the total $PM_{2.5}$ and $PM_{2.5-10}$ mass measured by gravimetry. Regression analysis of estimated mass vs. mass obtained by gravimetry presented correlation coefficients of 0.84 and 0.75, and slopes of 0.73 and 0.45, for $PM_{2.5}$ and $PM_{2.5-10}$, respectively (Figs. 3c and 4c). Results revealed that complete mass closure was rarely achieved in the samples, and there was often an important discrepancy between chemical and gravimetric masses. Particle chemical composition data on $PM_{2.5}$ and PM_{10} measurements obtained in other studies (Tsyro, 2005; Chan et al., 1997; Harrison et al., 2003; Andrews et al., 2000) showed identical conclusions.

4. Discussion

An atmospheric aerosol mass chemical balance risks being incomplete even when a very wide number of constituents is analyzed. Conversion of the latter to aerosol mass is problematic since elements such as oxygen, nitrogen and hydrogen should be estimated because usually they are not determined in the water insoluble aerosol fraction.

Approximations associated with the estimation of the organic matter amount and with the composition of the crustal materials, were considerably simplified and contain high uncertainties.

The assumed organic matter/organic carbon concentration ratio of 1.6 may be low, leading to underestimation of the true organic concentration in the sample. According to Saxena et al. (1995), for many oxygenated organic compounds expected to be found in atmospheric particles, the average molecular weight/carbon weight ratio ranges between 1.3 and 3.75.

In the estimation of crustal material only 10 compounds were used to determine the soil contribution. However, other compounds might be present. For instance Na_2O and MgO also contribute to the earth's crust in approximately 3% each (Andrews et al., 2000). In addition not all metals referred come only from dust (principally Co and Ca) and not all metals in dust are solely present as oxides. For instance, in this study the carbonates were not measured. The maximum possible carbonate mass present is 1.5 times the mass of calcium (the ratio of the carbonate and calcium ionic weights in calcium carbonate—the most common geological

form). This is an upper limit for actual carbonate levels, since in surface soils Ca is most commonly present in oxide forms such as CaO (Chow and Watson, 2002). Considering that all calcium is present as carbonate the measured and estimated species explanation increase to, respectively, 85% and 72% for the total PM_{2.5} and PM_{2.5–10} mass measured by gravimetry.

Another possible cause for obtaining slopes lower than unity in the fitting of mass balance and gravimetrically measured total aerosol mass is the presence of water in hydrate forms. Considering the levels of relative humidity encountered and PM composition, hydrates can be formed from water vapor attracted by the hydrophilic components of the sampled particles and incorporated in a matrix of molecules or ions. Therefore, if the water concentration is not high enough to yield a liquid solution, water molecules are incorporated into the solid-phase compounds and result in hydrates (Baumann et al., 2003). Thus, the gravimetrically measured particle mass does not necessarily represent dry PM_{2.5} and PM_{2.5–10} mass. According to Tsyro (2005), depending on particle composition, particle-bound water constitutes 20–30% of the annual mean PM₁₀ and PM_{2.5} concentrations, which is consistent with the experimental estimates in this work.

Other possible cause for lack of closure is the fact that gravimetric measurement did not accurately represent the Gent samples analyzed chemically due to differences in the inlet size cutting curves for different samplers.

Figs. 5 and 6 show that the temporal variation of the source contributions obtained by the PCA/MLRA and MBA was very similar for most of PM sources, since a high daily inter correlation between methods was observed. However, quantitatively some discrepancies were detected.

The contribution of identified sources to PM_{2.5} and PM_{2.5–10}, calculated with the PCA-MLRA, was generally higher than with MBA. This fact means that this method accounted for a larger fraction of PM than MBA. The regression analysis of estimated mass by MLRA vs. mass obtained by gravimetry results in correlation coefficients of 0.84 and 0.92, and slopes of 0.84 and 0.92, for PM_{2.5} and PM_{2.5–10}, respectively.

The origin of the differences in the source contributions obtained by the MLRA and MBA lies in their own method characteristics. In the PCA-MLRA methodology, the bulk PM concentrations are distributed among the identified sources as a function of the degree of correlation between the source tracers and the PM mass. The MLRA method accounts for a larger fraction of PM than the MBA because a larger proportion of PM which has not been accounted for (uncounted species) is distributed among the identified sources. While in the

MLRA only one tracer is enough to represent the contribution of the source, MBA needs the measurement of (almost) all constituents associated with it.

5. Conclusion

The MBA was used to check data consistency, to characterize the relative contribution of different components to PM and to reassess the plausibility of common assumptions used in the literature to estimate particle composition from chemical measurements. Results revealed that full mass closure was rarely achieved, and there was often a discrepancy between chemical speciation and bulk gravimetric masses. Their possible causes could be related to 1) particle-bound water, 2) measurements artefacts due to the use of two different samplers and 3) uncertainties in the calculations of unmeasured species.

The latter is a MBA limitation, overpassed by the PCA/MLRA where non-measured compounds are partially distributed among the identified sources as a function of the degree of correlation between the source tracers and the non-measured PM mass. Therefore, probably more realistic information about the contribution of the sources could be extracted.

PM size distribution gives important information about sources (natural vs anthropogenic), being important to associate species in groups with the same provenance.

The estimated source contributions using the PCA/MLRA are highly correlated with MBA results. Both techniques concluded that the largest fine particle components were secondary aerosols and organic carbon; and geological and marine materials were the largest components of coarse particles.

The complementary of the MBA and PCA/MLRA approaches are very helpful in the determination of sources contribution for PM concentration and composition. The best estimation of the source contributions is probably bound by these two methods with the PCA/MLRA providing an upper bound and MBA a lower bound.

References

- Almeida SM. Composition and sources of atmospheric aerosol in an urban/industrial region. PhD thesis. University of Aveiro, Portugal (in portuguese), 2004.
- Almeida SM, Reis M, Freitas MC, Pio CA. Quality assurance in elemental analysis of airborne particles. Nucl Instrum Methods Phys Res B 2003a;207:434–46.
- Almeida SM, Freitas MC, Reis MA, Pio CA. Quality assessment on airborne particulate matter of *k*₀-INAA. J Radioanal Nucl Chem 2003b;257:609–13.

- Almeida SM, Pio CA, Freitas MC, Reis MA, Trancoso MA. Source apportionment of fine and coarse particulate matter in a sub-urban area at the Western European coast. *Atmos Environ* 2005;39:3127–238.
- Andrews E, Saxena P, Musarra S, Hildemann LM, Koutrakis P, McMurry PH, et al. Concentration and composition of atmospheric aerosols from the 1995 SEAVS experiment and a review of the closure between chemical and gravimetric measurements. *J Air Waste Manag Assoc* 2000;50:648–64.
- Baumann K, Ift F, Zhao JZ, Chameides WL. Discrete measurements of reactive gases and fine particle mass and composition during the 1999 Atlanta supersite experiment. *J Geophys Res* 2003;108 (D7):8416.
- Bowen HJM. Environmental chemistry of the elements. London: Academic Press; 1979.
- Bowen HJM, Gibbons D. Radioactivation analysis. Oxford: Clarendon; 1963.
- Burnett RT, Dales R, Krewski D, Vincent R, Dann T, Brook JF. Association between ambient particulate sulfate and admissions to Ontario hospitals for cardiac and respiratory diseases. *Am J Epidemiol* 1995;142:15–22.
- Chan YC, Simpson RW, Mctainsh GH, Vowles PD, Cohen DD, Bailey GM. Characterisation of chemical species in PM_{2.5} and PM₁₀ aerosols in Brisbane, Australia. *Atmos Environ* 1997;31 (22):3773–85.
- Chan YC, Simpson RW, Mctainsh GH, Vowles PD, Cohen DD, Bailey GM. Source apportionment of PM_{2.5} and PM₁₀ aerosols in Brisbane (Australia) by receptor modelling. *Atmos Environ* 1999;33:3251–68.
- Chow JC, Watson JG. Ion Chromatography in elemental analysis of airborne particles. In: Landsberger S, Creatchman M, editors. Elemental analysis of airborne particles. Advances in Environmental, Industrial and Process Control Technologies. USA: Gordon and Breach Sciences Publishers; 1999. p. 97–137.
- Chow JC, Watson JG. PM_{2.5} carbonate concentrations at regionally representative interagency monitoring of protected visual environment sites. *J Geophys Res* 2002;107(D21):8344–52.
- De Corte F. The k_0 -Standardization Method—A move to the optimization of neutron activation analysis. Agregé thesis. Gent University, Belgium, 1987.
- Dockery DW, Pope CA, Xu X, Spengler JD, Ware JH, Fay ME, et al. An association between air pollution and mortality in six US cities. *N Engl J Med* 1993;329(24):1753–9.
- Duarte RM, Santos EB, Pio CA, Duarte AC. Comparison of structural features of water-soluble organic matter from atmospheric aerosols with those of humic substances from aquatic environments. *Environ. Sci. Technol.*, submitted for publication.
- Freitas MC, Farinha MM, Ventura MG, Almeida SM, Reis MA, Pacheco AMG. Atmospheric selenium in an industrialised area of Portugal. *J Radioanal Nucl Chem* 2005;263(3):711–9.
- Grohse PM. Trace element analysis of airborne particles by atomic absorption spectroscopy, inductively coupled plasma-atomic emission spectroscopy, and inductively coupled plasma-mass spectroscopy. In: Landsberger S, Creatchman M, editors. Elemental analysis of airborne particles. Advances in Environmental, Industrial and Process Control Technologies, vol. 1. USA: Gordon and Breach Sciences Publishers; 1999. p. 1–65.
- Harrison RM, Pio CA. Size-differentiated composition of inorganic atmospheric aerosols of both marine and polluted continental origin. *Atmos Environ* 1983;17(9):1733–8.
- Harrison MH, Jones AM, Lawrence RG. A pragmatic mass closure model for airborne particulate matter at urban background and road sites. *Atmos Environ* 2003;37:4927–33.
- Johansson SAE, Campbell JL. PIXE — A novel technique for elemental analysis. NY: Wiley; 1988.
- Maenhaut W. The “Gent” stacked filter unit (SFU) sampler for the collection of atmospheric aerosols in two size fractions: description and instructions for installation and use. IAEA CRP E4.10.08, Belgium, 1992.
- Mason B, Moore CB. Principles of Geochemistry. New York: Wiley; 1982. p. 46.
- Pio CA, Lopes DA. Chlorine loss from marine aerosol in a coastal atmosphere. *J Geophys Res* 1998;103(D19):25263–72.
- Pio CA, Castro LM, Ramos MO. Differentiated determination of organic and elemental carbon in atmospheric aerosol particles by a Thermal-optical method. In: Angeletti G, Restelli G, editors. Proceedings of the Sixth European Symposium on Physical–Chemical Behaviour of Atmospheric Pollutants, Report EUR 15609/2 EN; 1993. p. 706–11.
- Pio CA, Castro LM, Cerqueira MA, Santos IM, Belchior F, Salgueiro ML. Source assessment of particulate air pollutants measured at the southwest European coast. *Atmos Environ* 1996;30(19):3309–20.
- Pope CA. Respiratory hospital admission associated with PM₁₀ pollution in Utah, Salt Lake, and Cache Valleys. *Arch Environ Health* 1991;46:90–7.
- Pope CA, Burnett RT, Thun MJ, Calle EE, Krewski D, Ito K, et al. Lung cancer, cardiopulmonary mortality, and long-term exposure to fine particulate air pollution. *J Am Med Assoc* 2002;287 (9):1132–41.
- Putaud J-P, Raes F, Van Dingenen R, Brüggemann E, Facchini M-C, Decesari S, et al. A European aerosol phenomenology-2: chemical characteristics of particulate matter at kerbside, urban, rural and background sites in Europe. *Atmos Environ* 2004;38:2579–95.
- Rodríguez S, Querol X, Alastuey A, Plana F. Sources and processes affecting levels and composition of atmospheric aerosol in the Western Mediterranean. *J Geophys Res-Atmos* 2002;107 (D24):4777.
- Roemer W, Hoek G, Brunekreef B. Effect of ambient winter air pollution on respiratory health of children with chronic respiratory symptoms. *Am Rev Respir Dis* 1993;147:118–24.
- Saxena P, Hildemann LM, McMurry PH, Seinfeld JH. Organics alter hygroscopic behaviour of atmospheric particles. *J Geophys Res* 1995;100:18755–70.
- Schwartz J, Morris R. Air pollution and hospital admission for cardiovascular disease in Detroit, Michigan. *Am J Epidemiol* 1995;142:22–35.
- Schwartz J, Dockery DW, Neas LM. Is daily mortality associated specifically with fine particles? *J Air Waste Manag Assoc* 1996;46:927–39.
- Seinfeld JH, Pandis SN. Atmospheric chemistry and physics – From air pollution to climate change. John Wiley & Sons, inc. Wiley Interscience, 1998.
- Sternbeck J, Åke S, Kenth A. Metal emission from road traffic and the influence of resuspension—results from two tunnel studies. *Atmos Environ* 2002;36:4735–44.
- Tanner RL, Marlow WH, Newman L. Chemical composition of size-fractionated sulfate in New York aerosol. *Environ Sci Technol* 1979;13:75–8.
- Thurston GD, Spengler JD. A multivariate assessment of meteorological influences on inhalable particle source impacts. *J Clim Appl Meteorol* 1985;24:1245–56.

- Tsyro SG. To what extent can aerosol water explain the discrepancy between model calculated and gravimetric PM_{10} and $PM_{2.5}$. *Atmos Chem Phys* 2005;5:515–32.
- Turpin BJ, Lim H-J. Species contributions to $PM_{2.5}$ mass concentrations: revisiting common assumptions for estimating organic mass. *Aerosol Sci Tech* 2001;35:602–10.
- Van Dingenen R, Raes F, Putaud JP, Baltensperger U, Charron A, Facchini MC, et al. A European aerosol phenomenology-1: physical characteristics of particulate matter at kerbside, urban, rural and background sites in Europe. *Atmos Environ* 2004;38:2561–77.
- Weatherburn MW. Phenol-hypochlorite reaction for determination of ammonia. *Anal Chem* 1967;39(8):971.