

Chemical Elements in Airborne Particulate Matter at Pico Mountain, Azores Island (Portugal) in Period from August 2008 to June 2009

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Abstract — Airborne particulate matters with particles $\leq 10 \mu\text{m}$ in aerodynamic diameter (PM_{10}) were collected on quartz-fibre filters from 7 August 2008 to 18 June 2009 at Pico Mountain, Azores Island (Portugal). The samples were analyzed by the k_0 -based instrumental neutron activation analysis (k_0 -INAA) technique at the Portuguese research reactor. A total of 21 elements: As, Ba, Br, Ce, Co, Cr, Eu, Fe, Hf, K, La, Mo, Na, Sb, Se, Sc, Sm, Th, U, Yb and Zn were determined in the airborne PM_{10} 's and used as independent variables in the problem of factor analysis by the positive matrix factorization (PMF) method. The backward trajectory analysis using HYSPLIT (atmospheric modeling software) and the calculation of enrichment factors associated with the PMF were performed to identify the PM sources and to estimate their contributions to the particle mass concentrations. The results based on the data set in the studied period indicated that major sources contributed to airborne PMs at the Pico Mountain were soil, sea-salt, combustion and dust. The best solutions were found to be five factors for elemental compositions of the particulate matters. The comparison of the results in the present studied period with the previous obtained ones at the same sampling site has been presented and discussed to which the results have again confirmed that the Pico Mountain is a valuable sampling site for studies of long-range impact of source regions, particularly, the north and central American regions.

Keywords — Airborne Particulate Matter, Enrichment Factor, HYSPLIT Model, k_0 -INAA, PICO-NARE Observatory, Positive Matrix Factorization.

1 INTRODUCTION

Many atmospheric observatories are located on mountains, with the aim of observing conditions in the free troposphere (FT). Such observations are valuable for studies of long-range impacts of source regions. The Pico Mountain station (also known as PICO-NARE) is an air pollution observatory. Measurements at Pico Mountain are able to study the free atmosphere (not directly affected by the ocean) and see pollution transport events originating in North America and Europe. The station was developed to study the global impacts of human activities on the atmosphere. It has also proven valuable for learning about the effects of large wild fires in North America and even Siberia [1].

The PICO-NARE station was originally developed to study the impacts of continental air pollution outflow upon the atmosphere over the North Atlantic Ocean, Europe, and downwind regions. However, research at the station has led to important findings on several topics. These findings were summarized

in references [2-5].

The study on chemical composition of airborne PMs with particles $\leq 10 \mu\text{m}$ in aerodynamic diameter (PM_{10}) collected at the PICO-NARE sampling site was begun in early 2000s [Freitas et al., 2007]. In these studies, the data set was based on samples collected before 2007. Recently, samples have continuously been collected and the determinations of elemental composition in these samples were completed. Moreover, the EPA PMF V3.0 software [6] developed by the US Environmental Protection Agency has recently been applied in our laboratory. Therefore, the objectives of this work are to 1) Characterize the elemental composition in airborne PMs collected in the period from 7 August 2008 to 18 June 2009 at PICO-NARE; 2) Identify the PM sources and estimate their contributions to the particle mass concentrations; 3) Compare the previous obtained results with the results obtained in the present study.

2 EXPERIMENTAL

2.1 Site characteristics and sampling

The PICO-NARE station is located on the summit Caldera of Pico mountain, an inactive volcano on Pico Island in the Azores, Portugal (38 degrees,

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28.226 minutes N latitude, 28 degrees, 24.235 minutes W longitude, 2225 m altitude) (Fig. 1). A total of 88 PM₁₀ samples were collected on quartz-fibre filter tapes (Manufacturer: Pallflex[®]; Type: Q250F) using a high volume air sampler (a seven-wavelength Aethalometer - model AE31) at a flow rate around 0.65 m³ min⁻¹ for 24 h each sample in the period from 7 August 2008 to 18 June 2009. Total volume of air passed through the filter tapes was computed using the flow recorder. The samples for analysis (blanks and exposed filters) were cut from the strips in circular forms with an area of 0.950 ± 0.086 cm² each. The exposed side of each spot was covered with a piece of unexposed blank filter, to avoid contamination of the sample with the polyethylene top cover; the same procedure was applied to each blank in order to obtain identical geometry. More details about the filters can be found in our previous publications [7]. All samples were packed into aluminum sheets for the neutron irradiation on the Portuguese research reactor (RPI).



Fig. 1. Location of Azores Island on the world map

2.2 Elemental composition

The elemental concentrations of the PM₁₀ samples were analyzed by the *k*₀-based instrumental neutron activation analysis (*k*₀-INAA) using RPI. The samples (blanks, filters and reference materials) together with the Au monitors in disk shape (0.125 mm thickness; 5 mm diameter) of a 0.1% Au-Al alloy (usually three Au monitors positioned at top, middle and bottom of irradiation containers) were irradiated for 7 h at Cell 55 of RPI with a thermal neutron flux ~8.4 × 10¹² cm⁻² s⁻¹. The samples after irradiation were allowed to decay for 2-3 days and 3-4 weeks prior to performing the first and second measurements for 7 h and 15 h, respectively, for each sample. The Au monitors were measured after 7 days of decay and the neutron flux distribution in the irradiation container was derived from the top, middle and bottom Au monitors. The Au monitors and samples were measured on the calibrated HPGe detectors with the energy resolution (FWHM) approximately 1.85 keV at 1332.5 keV and the relative efficiency of 30%. All measurements were automatized using the ORTEC[®] ASC-2 systems.

The *k*₀-IAEA software was used for extracting the analytical results in terms of elemental concentrations, accuracies and detection limits. A total of 21 elements: As, Ba, Br, Ce, Co, Cr, Eu, Fe, Hf, K, La, Mo, Na, Sb, Sc, Se, Sm, Th, U, Yb and Zn was determined in the airborne PM filters. However, only 18 elements (except As, Ba and Se in the above list) were used to study in this work since the three elements were more than 90% of samples below the detection limit. The QA/QC result by *k*₀-INAA at our laboratory was reported in the previous studies [8-10]. Generally speaking, the relative biases of the analytical results as compared with the certified values in the used reference materials were mostly within 12%.

2.3 Backward trajectory

Atmospheric transport patterns were evaluated by examining 5-day backward trajectories originating from the building on each day wind plume was recorded at the PICO-NARE station. The entire path of each trajectory was evaluated to determine a path of transit for the air parcels. The HYSPLIT model [11] provided information as to the origin of the air at the rooftop level. We initiated each trajectory at three altitudes (100m, 500m and 1000m) to simulate air at the rooftop of the PICO-NARE location. An example of a 5-day backward trajectory is displayed in Fig. 2.

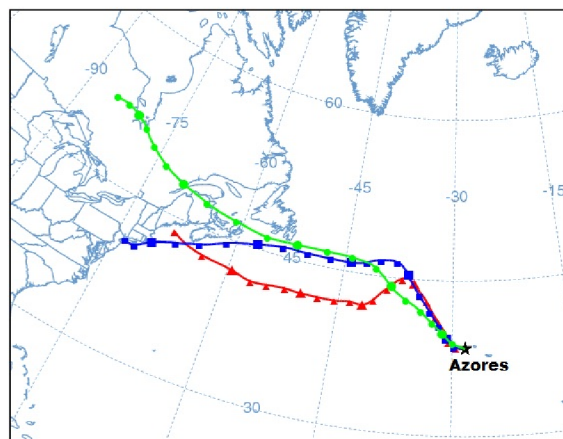


Fig. 2. A 5-day backward trajectory ending on 6 June 2009 (12:00 UTC), vertical motion: Isentropic at PICO-NARE.

2.4 Enrichment factor

The crustal enrichment factor method has been largely used to evaluate how much the sample composition reflects a typical bulk crustal composition, and this can be done by normalizing the concentration values in relation to a reference element. Considering Sc as a reference, the enrichment factors EF_{Sc} were calculated as:

$$EF_{Sc} = \frac{[C_x / C_{Sc}]_{Sample}}{[C_x / C_{Sc}]_{BulkSoil}} \quad (1)$$

where, C_x and C_{Sc} are concentration of elements x and Sc, respectively. The bulk soil composition used in this study was taken from [13]. The calculated results for EF_{Sc} are shown in Fig. 2.

2.5 Positive matrix factorization

It was well-known that, in order to identify sources, multivariate receptor modeling can be applied to the observed PM composition data. Multivariate approaches are based on the idea that the time dependence of a chemical species at the receptor site will be the same for species from the same source. Chemical compositions (species) are measured in a large number of samples gathered at a single receptor site over time. Species of similar variability are grouped together in a minimum number of factors that explain the variability of the data set. It is assumed that each factor is associated with a source or source type. Among the multivariate receptor modeling used for aerosol source identification, positive matrix factorization (PMF) is a power technique developed by Paatero and Tapper [14]. PMF has special features of the use of realistic error estimates to weight the data values and the imposition of non-negativity constraints in the factor computational process. The application of PMF have been successful in several atmospheric studies [15].

The general receptor modeling problem can be stated in terms of the contribution from p independent sources to all chemical species in a given sample as follows:

$$x_{ij} = \sum_{k=1}^p g_{ik} f_{kj} + e_{ij} \quad (2)$$

where x_{ij} is the j th species concentration measured in the i th sample, g_{ik} is the particulate mass concentration from the k th source contributing to the i th sample, f_{kj} is the j th species mass fraction from the k th source, e_{ij} is residual associated with the j th species concentration measured in the i th sample, and p is the total number of independent sources. The corresponding matrix equation is:

$$X = GF + E \quad (2)$$

where X is an $n \times m$ data matrix with n measurements and m number of elements; E is an $n \times m$ matrix of residuals; G is an $n \times p$ source contribution matrix with p sources; and F is a $p \times m$ source profile matrix. There are an infinite number of possible solutions to the factor analysis problem (rotations of G matrix and F matrix). To decrease rotational freedom, PMF uses nonnegativity constraints on the factors. The parameter FPEAK is used to control the rotations. PMF provides a solution that minimizes an object function, $Q(E)$, based on uncertainties for each observation.

3 RESULTS AND DISCUSSION

Statistics of elemental concentrations for 88 PM₁₀ samples collected at Pico mountain in the period from 7 August 2008 to 18 June 2009 is summarized in Table 1.

Table 1. Statistics of elemental concentrations (ng m⁻³)

Element	Min	Max	AM	GM	SD	n
Br	0.2	18.9	3.5	2.1	3.8	79
Ce	0.03	3.73	0.28	0.24	0.38	15
Co	0.01	1.74	0.34	0.26	0.3	21
Cr	0.01	75.56	2.24	0.59	8.82	42
Eu	0.001	1.568	0.053	0.028	0.167	11
Fe	9	1625	108	65	224	34
Hf	0.001	0.067	0.013	0.010	0.011	26
K	5	330	64	46	64	39
La	0.002	2.224	0.184	0.096	0.292	65
Mo	0.01	17.32	1.33	0.82	2.47	30
Na	2	475412	7730	990	50824	88
Sb	0.6	22.8	9.3	8.2	5.0	29
Sc	0.001	0.358	0.026	0.012	0.053	38
Sm	0.001	0.083	0.016	0.012	0.015	42
Th	0.004	0.097	0.021	0.02	0.01	9
U	0.001	0.129	0.029	0.027	0.015	11
Yb	0.01	0.17	0.03	0.02	0.02	12
Zn	0.5	294.1	8.0	4.1	31.3	26

“AM” – Arithmetic mean; “GM” – Geometric mean; “SD” – Standard deviation; “n” – Number of samples.

As compared with the previous results [7, 16], the mean of elemental concentrations of the sampling period 2001-2004 decreased a factor of 26.9, 10.2, 9.6, 8.8, 4.9, 2.5, 2.5, 2.4, 2.1, 1.3 and 1.3 for U, Mo, Hf, Sm, Br, Fe, Sb, Co, Sc, Zn and La, respectively, in comparison with the period 2008-2009. Especially, only Na increased a factor of 16.2.

Summary of the contributions of elemental concentrations according to trajectories categorized with five directions: North-Central America (N-C Am), Central-South America (C-S Am), Africa, Europe and Ocean (not clear direction during 5 days traced), is shown in Table 2.

Table 2. Contribution of elemental concentrations according to trajectories (in percentage)

Element	N-C Am	C-S Am	Africa	Europe	Ocean
Br	30.41	-	0.09	2.28	67.22
Ce	20.59	-	4.25	-	75.16
Co	49.67	-	-	16.78	33.55
Cr	25.81	-	0.08	4.61	69.50
Eu	0.65	-	-	-	99.35
Fe	18.60	-	-	1.03	80.37
Hf	65.68	-	1.19	5.92	27.20
K	31.67	-	0.10	7.25	60.97
La	38.46	-	0.22	2.15	59.18
Mo	69.35	-	-	-	30.65
Na	11.65	-	0.09	4.17	84.09
Sb	44.87	-	-	6.55	48.58
Sc	24.03	-	-	2.04	73.93
Sm	64.70	-	1.75	0.40	33.16
Th	39.84	-	-	-	60.16
U	51.74	-	-	13.61	34.65
Yb	11.27	-	-	24.26	64.48
Zn	14.90	-	-	4.54	80.56

“-” denotes for not detected

The results in Table 2 indicated that two directions contributing the most air parcels to PICO-NARE during the studied period might be ocean and north-central America in which the former one is ranging between 30.65% (Mo) and 99.35% (Eu) and the later is ranging between 0.65% (Eu) and 69.35% (Mo). The European direction might be contributing the less ranging between 0.40% (Fe) and 24.26% (Yb) while the African direction the least is ranging between 0.09% (Br and Na) and 4.25% (Ce). Particularly, the central-south direction seems to be none contributing during entire studied period. These results suggested that the airborne PM₁₀'s collected at PICO-NARE were mainly brought by sea around and from north-central America.

Enrichment factors EF_{Sc} higher than 10 (Fig. 3) can be observed for As, Cr, Eu, Zn, Na and Sb.

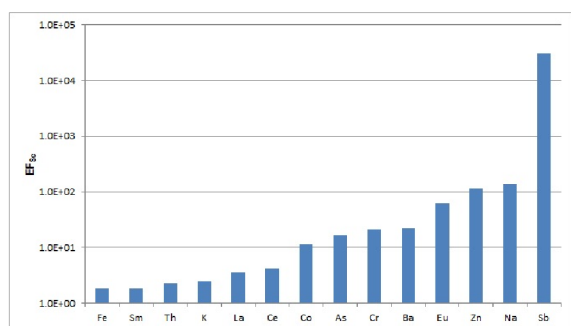


Fig. 2. Enrichment factor using Sc as a reference element

As for the application of PMF, the data set was prepared so that data below the reported detection limit for each species were substituted with one half of the detection limit and their overall uncertainties were set at five sixth of the detection limit values. The missing data were substituted with the geometric mean value and their accompanying uncertainties were set at four times this geometric mean values [10].

EPA PMF V3.0 was applied to the PM₁₀ particulate species from which four main sources were identified as sea-salt, soil, combustion and dust. The best solutions were found to be five factors for elemental compositions of the particulate matters. The factor profiles of elements generated from the PMF performed on the data set are shown in Table 3.

Table 3. Factor profiles (%) of elements in PM₁₀ collected at Pico Mountain in period August 2008-June 2009

Element	Sea	Soil	Combustion	Dust
Na	94.47			
Fe	2.68	72.12		34.24
Sb	0.61			
Zn	0.18	0.86	12.85	1.94
Mo		2.09	1.12	
Cr			0.97	2.43
Ce				
Co				0.62
Sm				
Th				

Hf				
La				
Yb				0.06
Eu				
Br		0.42	84.87	0.43
K	1.97	24.36		59.97
Sc				
U			0.09	

In Table 3, the factor profile of Na (94.47%) was the most which may be associated to sea-salt source. The factor profiles of Fe (72.12% and 34.24%) may be associated to soil and dust sources, respectively. The factor profiles of Br (84.87%) may be associated to combustion source and of K (24.36% and 59.97%) seem to be associated to soil and dust sources, respectively.

Seasonal contribution of sources in the period of August 2008 – July 2009 is shown in Fig. 3, where the source contribution in Spring is higher a factor of 1.38 than Summer.

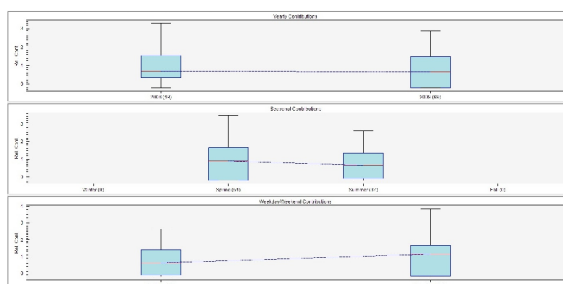


Fig. 3. Seasonal contribution of sources in period of August 2008 – July 2009

Finally, the Q values and factor identifications for stability and the interquartile ranges around the profiles were examined through the bootstrapping statistics for the final solution (Fig. 4).

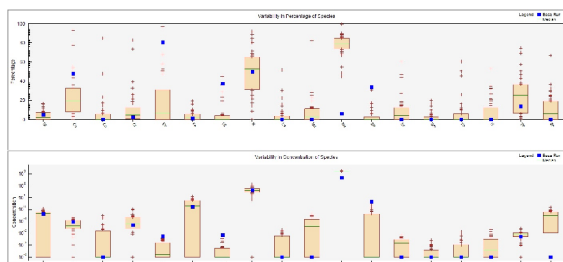


Fig. 4. The bootstrap factor expressing for the variability in percentage of species (above) and the variability in the concentration of each species (below).

4 CONCLUSIONS

The PM₁₀ compositional data measured at a monitoring site in Pico Mountain were characterized through the determination of chemical elements by the k_0 -INAA technique at RPI, thence, the data set was interpreted by using several tools in order to identify the PM sources and to estimate their contributions to the particle mass concentrations, i.e. using PMF, enrichment factors and backward

trajectories. The PMF effectively resolved five sources for the PM₁₀'s. Na contributed the most, which is identified as sea-salt source. This source impact is higher in Spring. Fe contributed the third which is identified as soil source. The impact from the soil source is graphically seen using EPA PMF V3.0 software. Combustion source was estimated by the contribution of Br to the PM₁₀ which is evaluated the second. The contribution of K is the least assigned to dust source that might be transited by Saharan dust. The results have again confirmed that the Pico Mountain is a valuable sampling site for studies of long-range impact of source regions, particularly, the north and central American regions. The mean of concentration of elements, i.e. U, Mo, Hf, Sm, Br, Fe, Sb, Co, Sc, Zn and La in the sampling period 2001-2004 decreased in comparison with the period 2008-2009, while only Na increased. This is suggesting that another study using entire data set so far should be conducted and the results would be published in the next paper.

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