ELSEVIER
Nuclear Instruments and Methods in Physics Research B 189 (2002) 272–278
NIM B
Beam Interactions with Materials & Atoms
www.elsevier.com/locate/nimb

Comparison of continental Portugal and Azores Islands aerosol during a Sahara dust storm

M.A. Reis [a,b,*], O.R. Oliveira [a,b], L.C. Alves [a,b], E.M.C. Rita [a,b], F. Rodrigues [c], P. Fialho [c], C.A. Pio [d], M.C. Freitas [a], J.C. Soares [a,b]

[a] *ITN, Apartado 21, EN10 Sacavém, 2685-953 Sacavém, Portugal*
[b] *CFNUL, Av Gama Pinto No. 2, 1699 Lisboa, Portugal*
[c] *Department of Agrarian Sciences of the University of the Azores, 9701-851 Terra Cha Angra do Heroísmo, Azores, Portugal*
[d] *Department of Environment and Planning of the University of Aveiro, Campus de Santiago, 3810-193 Aveiro, Portugal*

Abstract

Airborne particulate matter plays an important role in the Earth's energy balance. One of the main reasons is that the real size of a significant number of the particles, mainly those of anthropogenic origin, is similar to the wavelength of visible light. Knowledge of the composition of such particles, as well as their dynamics and trajectories in the atmosphere is therefore very important. In the period from 23 February to 22 March 2000, a movement of airborne particulate matter going over Europe and towards Azores was identified based on satellite observation. This work presents a preliminary study based on PIXE and nuclear micro-probe analysis of samples collected during that period both in Portugal mainland and in Terceira Island in the Azores. Time-shifted correlation of sample composition and individual particle composition are presented and discussed. Results point to the possibility of inferring long-range transport of aerosol particles from the samples multi-element analysis, and to the existence of fractions of the North Atlantic aerosol identical at both Portugal mainland and Terceira Island. © 2002 Elsevier Science B.V. All rights reserved.

PACS: 89.60
Keywords: Aerosol; Azores; Long-range transport; Multi-element analysis; PIXE

1. Introduction

In a recent publication, Raes et al. [1] point out that the aerosol distribution and dynamics over the North Atlantic Ocean is complex. Data on aerosol composition, for both the Iberian Peninsula and the North Atlantic Ocean between the Portugese mainland and the Azores Islands are still rare. Since 1993 some work has been done on multi-element analysis of PM10 and PM2.5 aerosol using PIXE and INAA [2,3], but the combination of such measurements and meteorological studies is not common in the literature. This work presents a preliminary study aiming at the use of multi-element data in studies of air masses long-range transport. Data from backward and forward

---

[*] Corresponding author. Address: Department of Physics, ITN, EN10, 2686 Sacavém Codex, Portugal. Tel.: +351-21-9946107; fax: +351-21-9941525.
E-mail address: mareis@itn.pt (M.A. Reis).

PII: S0168-583X(01)01056-4

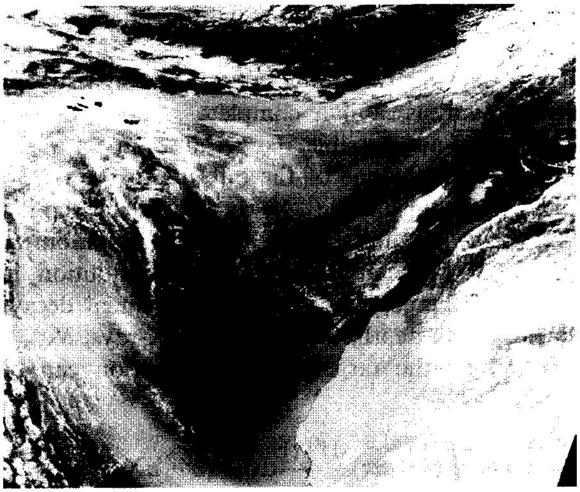

Fig. 1. Satellite data for 29 February 2000. Courtesy of SeaWiFS Project NASA/GSFC and ORBIMAGE. These data combined with backward trajectories calculations indicate that the mineral aerosol collected at the Azores (Terceira Island) in the period finishing on the 29th, is originated in the Magrebe Region. The transport is predicted to have occurred at heights between 50 and 4000 m. Forward trajectories calculations point to a possible contribution from aerosol originated in Portugal mainland.

air mass trajectories calculations were compared to data from PIXE analysis of aerosol samples collected at Faralhão (40 km to the South of Lisbon) and at Canada da Ajuda – Santa Bárbara, a place 50 m above sea level and located in Terceira Island, in the Azores Archipelago (geographical coordinates 38°43′48″ N, 27°19′18″ W). Samples were collected during a particular high aerosol density condition identified by satellite data and described as a Sahara dust storm. Fig. 1 presents a satellite picture representative of this situation, which is one of the typical North Atlantic Ocean aerosol conditions mentioned by Raes et al. [1].

The samples used in this work were originally collected in independent experiments. Nevertheless, data provided very interesting results, and give rise to important questions.

2. Experimental

At the Azores location samples were collected with a high-volume sampler Sierra PM10, model SSI 220, with a Sierra PM10 separation head. The air flux used was 1.13 m^3/min. The aerosol was collected in two fractions, below and above an equivalent aerodynamic diameter of 0.95 μm. The filters were quartz fibre filters (Whatman 20.3 × 25.4 cm^2 QM-A) which were pre-treated by acid washing followed by washing with ultra-pure water and then, in order to prevent organic contamination, filters were treated thermally at 750 °C in an oven for 6 h. The first stage of pre-treatment was carried out at the laboratory of the Department of Environment and Planning of the University of Aveiro following the procedures described by Tanner et al. [4]. Afterwards filters were grouped in sets of 10 and mailed to the Department of Agrarian Sciences of the Azores University, where the thermal treatment was carried out, two filters at a time placed over aluminium paper. Finally, the filters were weighed in a controlled RH environment before and after sampling in a Gibertini model E42 B-E42 S B electronic balance (0.0001 g accuracy).

At Faralhão, a Gent Aerosol Sampler [5] was used. Here, ITN has been sampling PM10 separated in two fractions, above and below 2.5 μm equivalent aerodynamic diameter, since 1995. The sampler uses a stacked filter unit loaded with Costar Nuclepore® membrane filters. The top filter has a pore size of 8 μm and the bottom one a pore size of 0.4 μm. The air flux used is 15 l/min, which assures the separation at 2.5 μm. Sampling is done in a week averaging mode [3] by having the pumping unit run only 10 min out of every 2 h and replacing the filters after a week of operation. The period covered by this study is from 17 February to 22 March 2000. In Table 1 the dates of sampling are presented; they do not completely match because the experiments were originally carried out independently.

The samples were analysed by PIXE at the ITN 3.1 MV Van de Graaff accelerator. Spectra were obtained with an Oxford Instruments 155 eV resolution Si(Li) detector, and analysed using the DATTPIXE package [6]. Quartz filters had to be studied as thick targets while Nuclepore® filters were treated as thin targets, as is common practice. Thus the data for the Azores samples were obtained as μg/g of analysed filter material, while data for Faralhão area are available in ng/m^3.

Table 1
Dates of start and end of sampling at each of the two stations

Reference	Start	End
Azores		
ACR1	23 February 2000	27 February 2000
ACR2	27 February 2000	29 February 2000
ACR3	2 March 2000	6 March 2000
ACR4	6 March 2000	10 March 2000
ACR5	10 March 2000	14 March 2000
ACR6	14 March 2000	18 March 2000
ACR7	18 March 2000	22 March 2000
Faralhão		
FAR255	17 February 2000	24 February 2000
FAR256	24 February 2000	3 March 2000
FAR257	3 March 2000	10 March 2000
FAR258	10 March 2000	17 March 2000
FAR259	17 March 2000	24 March 2000

One of the samples, namely ACR4, was also analysed in the ITN nuclear micro-probe, where the filter was analysed with the beam in a direction normal to the filter surface, and also parallel to the filter surface, for analysis of the filter cross-section.

3. Results and discussion

Fig. 2 presents the depth distribution of the sulphur and chlorine fine particles (<0.95 μm EAD) as determined by nuclear micro-probe analysis of a fine particles quartz filter cross-section. It can be seen that the particle deposition on the filter extends to at least 50 μm from the filter surface, with an inhomogeneous distribution along that depth. This distribution is a complicating issue for PIXE analysis, and a complete solution of this problem is not possible. To get an estimate of the analysed depth, one of the outputs of the DATTPIXE program [6], the "X-ray equivalent depth", $X_{eq.}$ for short, can be used. $X_{eq.}$ is the first moment of the X-ray emission intensity distribution in depth. If the concentration of an element decays linearly with depth, the number of X-rays, $N_{\text{X-rays}}$, emitted by the target under irradiation can be written as

$$N_{\text{X-rays}} = \int (b - ax)\frac{\mathrm{d}Y(x)}{\mathrm{d}x}\mathrm{d}x = (b - aX_{eq.})Y, \qquad (1)$$

assuming $Y(x)$ to be the yield of a homogeneous target. Now, the concentration reported by the DATTPIXE being the ratio between the number of measured X-rays, $N_{\text{X-rays}}$, and the yield, Y, will correspond to the concentration presented by the linear distribution at depth $X_{eq.}$, $(b - aX_{eq.})$. This value is of the same order of magnitude as the sample layer thickness from which information is being obtained during the PIXE analysis. In the filters analysed, the $X_{eq.}$ varied from 0.3 mg/cm^2 for Mg up to 3.3 for Pb mg/cm^2. The fine particle filter a real mass is roughly 75 mg/cm^2. Therefore only a fraction between 0.5% and 5% of the filter depth is analysed.

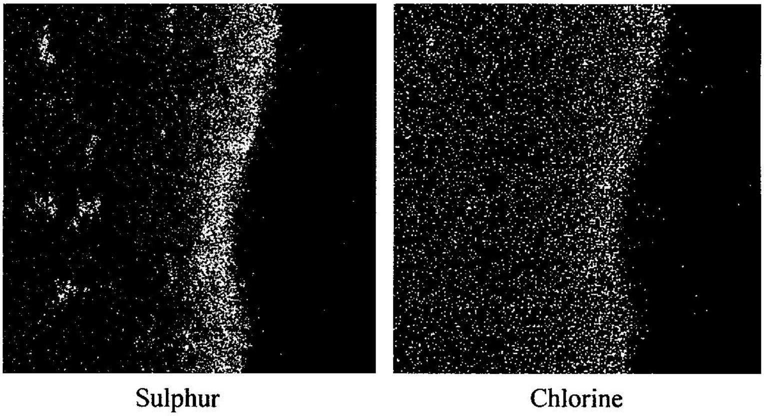

Fig. 2. Nuclear micro-probe PIXE analysis of the cross-section of ACR4 sample for particles having EAD < 0.95 μm. Scans are 500 × 500 μm^2.

Table 2
Statistics for the Azores and Faralhão samples[a]

Azores	Results in (μg/g)/m^3								
>0.95 μm	Count	Mean	Max.	Min.	<0.95 μm	Count	Mean	Max.	Min.
Mg	7	2.42E+00	5.08E+00	9.26E−01	Al	4	2.21E+00	3.74E+00	5.84E−01
Al	7	4.69E+00	1.14E+01	5.55E−01	Cl	7	9.15E−02	1.70E−01	2.12E−02
P	2	5.64E−02	6.81E−02	4.48E−02	K	7	3.05E−01	6.61E−01	2.40E−02
S	7	1.69E+00	2.48E+00	7.99E−01	Ca	7	3.78E−01	1.56E+00	3.48E−02
Cl	7	6.47E+00	1.42E+01	1.39E+00	Ti	6	3.46E−02	6.24E−02	1.44E−02
K	7	1.65E+00	4.44E+00	3.02E−01	V	3	3.90E−03	7.44E−03	2.08E−03
Ca	7	3.65E+00	1.44E+01	9.05E−01	Mn	2	5.34E−03	6.75E−03	3.93E−03
Ti	7	2.59E−01	6.78E−01	1.16E−02	Fe	7	1.37E−01	3.60E−01	2.69E−03
V	4	3.29E−02	5.90E−02	6.13E−03	Cu	7	4.13E−02	7.97E−02	1.64E−02
Cr	6	4.85E−03	9.93E−03	1.81E−03	Zn	7	1.55E−03	3.85E−03	1.19E−04
Mn	7	3.52E−02	1.00E−01	1.02E−03	Pb	1	1.57E−03	1.57E−03	1.57E−03
Fe	7	2.12E+00	6.16E+00	3.52E−02					
Ni	6	2.15E−03	4.09E−03	4.63E−04					
Cu	7	3.92E−01	1.11E+00	7.55E−02					
Zn	7	6.58E−03	1.34E−02	7.59E−04					
Br	7	9.70E−03	1.62E−02	7.14E−03					
Rb	5	6.50E−03	1.94E−02	1.13E−03					
Sr	7	2.25E−02	5.90E−02	6.69E−03					
Zr	7	1.12E−02	2.34E−02	3.27E−03					
Mo	4	4.41E−03	4.75E−03	4.18E−03					
Ba	6	1.13E−02	2.99E−02	1.83E−03					
W	7	2.17E−02	6.68E−02	2.25E−03					
Pb	7	4.13E−03	9.03E−03	1.61E−03					
Faralhão	Results in ng/m^3								
>2.5 μm	Count	Mean	Max.	Min.	<2.5 μm	Count	Mean	Max.	Min.
Mg	4	2.24E+02	3.06E+02	1.24E+02	Mg	3	1.20E+02	2.04E+02	6.31E+01
Al	5	7.36E+02	1.16E+03	3.58E+01	Al	5	4.75E+02	1.01E+03	9.45E+00
Si	5	1.64E+03	2.59E+03	1.20E+02	Si	5	1.04E+03	2.26E+03	3.64E+01
P	4	3.51E+01	5.31E+01	2.28E+01	S	5	7.44E+02	1.24E+03	2.17E+02
S	5	2.18E+02	3.30E+02	6.65E+01	Cl	4	4.89E+01	7.04E+01	1.82E+01
Cl	5	1.44E+02	4.23E+02	8.70E+00	K	5	1.76E+02	3.10E+02	3.27E+01
K	5	2.22E+02	3.32E+02	3.42E+01	Ca	5	3.03E+02	4.94E+02	7.77E+01
Ca	5	7.59E+02	1.10E+03	3.83E+02	Ti	5	1.45E+01	2.85E+01	1.99E+00
Ti	5	2.21E+01	3.27E+01	6.14E+00	V	3	3.77E+00	5.48E+00	2.21E+00
V	2	2.04E+00	2.15E+00	1.93E+00	Mn	5	3.81E+00	6.20E+00	1.43E+00
Mn	5	9.28E+01	4.44E+02	2.12E+00	Fe	5	1.83E+02	3.47E+02	3.54E+01
Fe	5	2.52E+02	4.77E+02	1.10E+00	Ni	5	2.44E+00	2.85E+00	1.41E+00
Ni	3	3.61E+00	8.34E+00	9.55E−01	Cu	5	4.44E+00	6.73E+00	2.62E+00
Cu	5	1.61E+01	4.00E+01	3.98E+00	Zn	5	3.27E+01	5.17E+01	1.38E+01
Zn	4	2.63E+01	5.42E+01	7.65E+00	Br	3	5.82E+00	6.22E+00	5.44E+00
Sr	4	1.57E+02	2.41E+02	6.03E+01	Pb	5	1.41E+01	1.93E+01	8.19E+00
Pb	1	8.37E+00	8.37E+00	8.37E+00					

[a] Data for Azores is expressed in (μg/g of analysed filter mass)/m^3. The exact conversion factor to ng/m^3 (the units of data from Faralhão) is dependent on the element and in the exact sample composition and geometry. This conversion factor is roughly of the order of 100.

Fig. 2 shows that the aerosol material is distributed more deeply in the filter than these analysed depths. For S the $X_{eq.}$ value is 0.5 mg/cm^2 and for Cl 0.55 mg/cm^2. The results obtained in this work must therefore be seen only as indicative. A comparison between concentration in filters from the Azores, and total suspended element mass, from Faralhão, is still possible because the amount of aerosol in the filter is always small relative to the filter mass. Thus the concentration in the filter normalized to the sampled volume is nearly proportional to the aerosol concentration in the atmosphere. The comparison between Azores and Faralhão was made using this assumption.

Statistics on the elemental atmospheric concentration for both fine particles (below 0.95 μm EAD for the Azores samples and 2.5 μm for the Faralhão samples), and coarse particles (the remaining part of PM10) are presented in Table 2.

Correlation coefficients between data from Faralhão and data from Azores, were then calculated for each element time series for the corresponding periods, but also for four possible time-shifted sequences. In Fig. 3 the results for S, Cl, Cu and Zn in fine particles are presented in graphical form. It appears that applying a one week delay to the S data from Faralhão a proportionality condition is obtained relative to Azores data. For Cl the same is seen for a two weeks delay, Cu correlates with a one week advance and Zn shows a correspondence for the same periods (no delay). For coarse particles data, correlation coefficients above 0.68 are found for Mg, Al, K, Ti, Mn, Cu and Zn for the corresponding periods.

These results seem to point to a fast moving mineral aerosol (it should be remembered that the samples correspond to week averages), in agreement with the satellite data. However, the fine particle component presents more complex behaviour, as different results are obtained for different elements.

In parallel to these measurements, backward and forward trajectories calculations were done using the HYSPLIT model [7]. These calculations

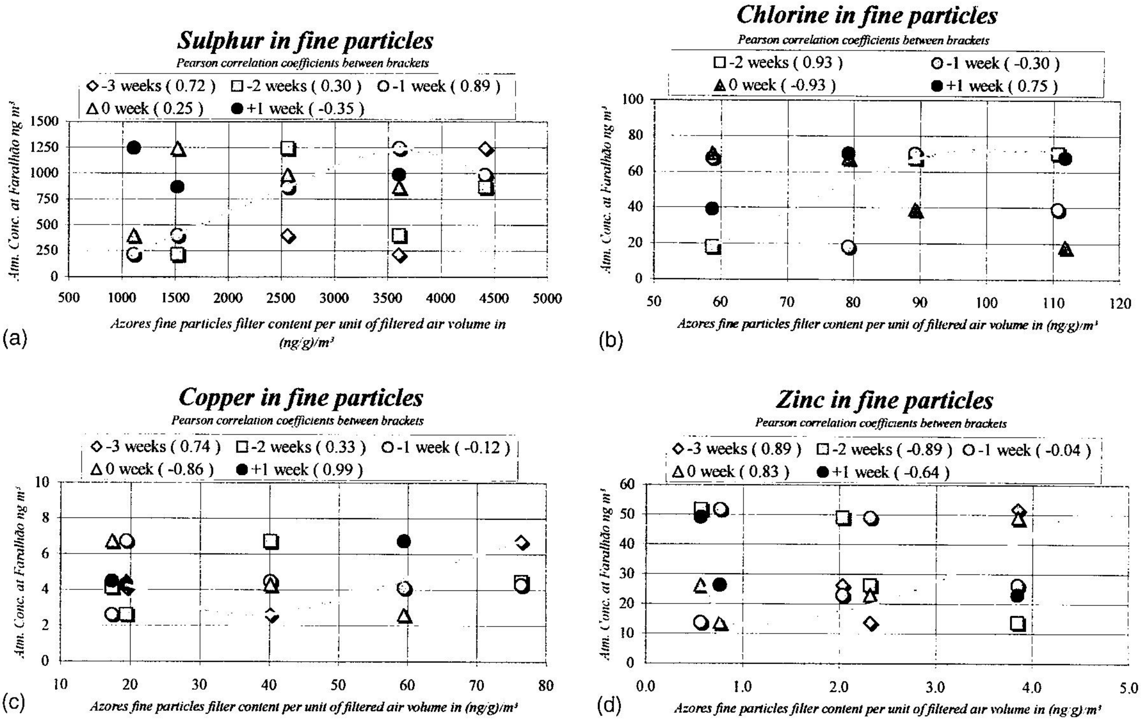

Fig. 3. Faralhão versus Azores data for S, Cl, Cu and Zn in fine particles. Concentrations in the filters normalized to the sampling volume is nearly proportional to the expectable atmospheric concentration in Azores atmosphere. Data series are referred to by the time difference between Azores time and Faralhão time references. The correlations identified are interpreted as indication of aerosol transport from Faralhão to Azores (negative time differences), from Azores to Faralhão (positive time differences), or that the concentrations should be similar within a week period (zero time differences). The grey line is intended only to guide the eye for the connection of the best correlation series.

were made from and to Azores and from and to Faralhão for periods up to 10 days, within the period of one month covered in this work. Air masses transfer within a single altitude calculation, point to delays of less than one week between Faralhão and Azores. Still, the results obtained show that the trajectories of air masses at low altitude are sometimes much different than those at high altitudes. If exchange of aerosol particles between different atmosphere levels is considered (due for instance to processes of entrainment) then transfer of airborne particles from Portugal mainland to the Azores and vice versa with delays of the order of one week or more may be explained. A possible "contamination" of the Saharan dust mineral aerosol with "polluted" fine aerosol from Europe, which may influence the results found in this work, is a very important issue [1].

Data from Fig. 3 still point to a puzzling result, namely the negative correlation coefficients found for Cl and Cu in the corresponding period. Following a different approach relative to the characterization of the aerosols in question here, one of the fine particle filter samples was studied using the Lisbon nuclear micro-probe (2 μm resolution). A typical particle is presented in Fig. 4. This was referred as a Cl/Cu particle. If the apparent size of this particle (shown in Fig. 4 to be of 15 μm in diameter) is its real size, then the particle should appear in the coarse particles filter, unless it has a very small density. The composition of the particle was determined by both PIXE (using GUPIX program [8]) and RBS (using DAN32 program [9]). The ratios of Cl to Cu and C to O are presented in Table 3. The results point initially to a $CuCl_2$ particle, but oxygen and carbon are also present.

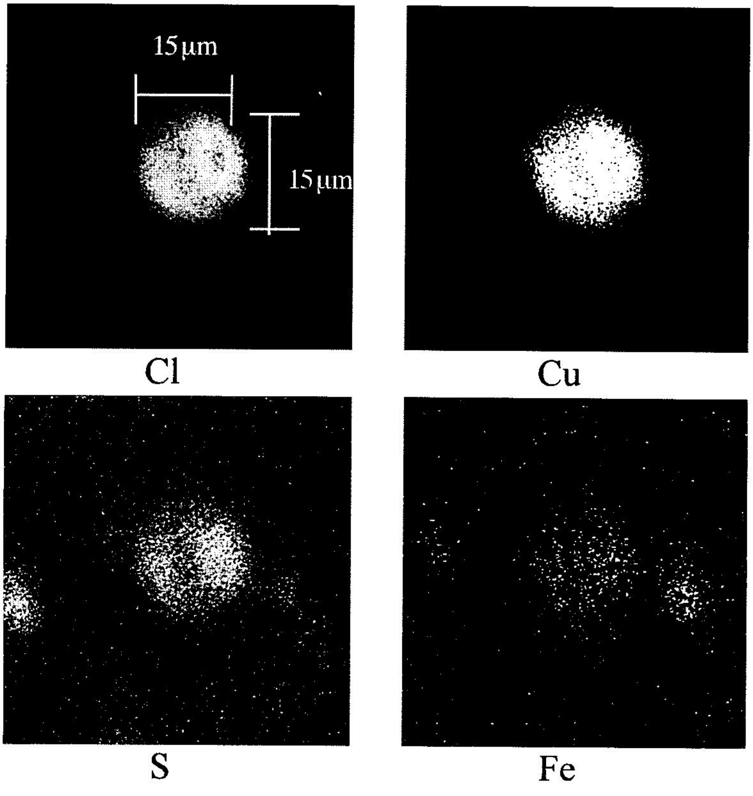

Fig. 4. X-ray elemental maps (scan 50 × 50 μm^2). A particle containing two lobes with Cl and Cu, presenting an overall size of 15 × 15 μm^2 is shown. Cl/Cu ratios obtained by PIXE and RBS point analysis of the lobes and central zone are presented in Table 3.

Table 3
Cl/Cu and C/O ratios determined for the zones of the particle presented in Fig. 3

Particle zone	Cl/Cu (atomic) *RBS fit*	Cl/Cu (atomic) *PIXE fit*	C/O (atomic) *RBS fit*
Bigger lobe	2	2	0.4
Central zone	2	1.7	0.4
Small lobe	2	1.7	0.6

In the central zone also N was found. These results may point to an organic nature or combination of organic and inorganic particles in an aggregation that provides the dynamic behaviour of a fine particle. At the same time these results also show that complex particle structures are found in particles sampled in the fine particles mode.

4. Conclusions

One of the most important results of this work is realizing that the combination of the three types of study presented here – trajectories calculations, macro-PIXE and micro-PIXE and micro-RBS – provides a significant insight into the dynamics of airborne particles transport in the atmosphere. By assessing both the semi-theoretical origin of aerosols (trajectories calculations) and the corresponding measured composition of the aerosol, the existence of unsuspected phenomena can be put in evidence (e.g., entrainment of particles transported at high altitudes). In the case of this work, the correlation between data collected at Faralhão and the Azores points to a condition of regional coarse aerosol, not verified in the fine particle component. In the case of the fine particle component, it might be even questioned whether there is a cycling of Cl and Cu (based on the existence of negative correlation coefficients of the corresponding period data which are accompanied by positive correlations on delayed data). Relative to Cl and Cu in the fine particles component, questions about their inclusion into organic based particles should also be raised based on the micro-beam analytical data.

Based on these conclusions, it can further be said that the approach presented in this work is a good methodological tool to access the dynamics of aerosol particles, air masses mixing, and long-range transport of pollutants. Therefore, the authors hope that this preliminary study may, most of all, open up the opportunity for long term detailed and exhaustive studies, which can be performed with relative small budgets as they mainly require the use of low cost equipment (like Gent samplers) and average-cost analytical methods (PIXE and nuclear micro-probe).

References

[1] F. Raes, R.V. Dingenen, E. Vignati, J. Wilson, J.-P. Putaud, J.H. Seinfeld, P. Adams, J. Atmos. Environ. 34 (2000) 4215.
[2] L.C. Alves, M.A. Reis, M.C. Freitas, M.A. Gouveia, X-ray Spectrom. 27 (1998) 313.
[3] L.C. Alves, M.A. Reis, M.C. Freitas, Nucl. Instr. and Meth. B 138 (1998) 941.
[4] R.L. Tanner, W.H. Marlow, L. Newman, Environ. Sci. Technol. 13 (1979) 75.
[5] P.K. Hopke et al., Aerosol Sci. Technol. 27 (1997) 726.
[6] M.A. Reis, L.C. Alves, Nucl. Instr. and Meth. B 68 (1992) 300.
[7] National Oceanic And Atmospheric Administration (NOAA), HYSPLIT4 (Hybrid Single-Particle Lagrangian Integrated Trajectory), Silver Spring, 1997.
[8] J. Maxwell, J.L. Campbell, W. Teesdale, Nucl. Instr. and Meth. B 43 (1989) 218.
[9] G. Grime, Presented at ICNMTA'96.