Identification of Sahara Sand Storms by PIXE, 1995 to 2006

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Abstract. Since 1995 airborne particle samples have been collected in Portugal in the framework of various campaigns and monitoring programs. Although small changes in sampling strategy occur, the possibility of building up a 12 years long data series lead to preparing a fully compatible set. One of the most remarkable results attained as a consequence of this effort, is the identification of various Sahara dust episodes based exclusively on PIXE data and statistical data analysis. During the whole 12 years period, events showing a Sahara signature are present with a different annual distribution, and evidence can be found for a time dependent fluctuation in the typical aerosol composition observed during these events. In a previous work it was seen that during this type of occurrences, aerosol composition at Azores and near Lisbon showed very high resemblance, mainly if small time delays were introduced in data prior to comparison. This implies that it seems realistic to assume that the aerosol being deposited over the whole South Eastern area of the North Atlantic due to Sahara dust events, are being subject to a fluctuating composition process, that may impact on the local ecosystem. Those results are compared to conclusions present in the literature related to the dynamics of airborne particles originated on the Sahara, and possible implications emerging from these comparisons are discussed.

Keywords: Sahara dust, Global Change, Airborne particles.

INTRODUCTION

One of the main sources of mineral aerosols is wind erosion of desert regions. In the case of aerosol originating in the Sahara region, it is estimated that it corresponds to nearly 50% of all mineral aerosol resuspended to the atmosphere each year. The effects of the Saharan aerosol spread very far. In fact, this aerosol, originated most probably in the Bodelé region, spreads over the whole North-Atlantic South-Easter area (NASE region) but also beyond it to the Caribbean, to the South of the United Kingdom and all over Europe and the Mediterranean [1,2]. The effects that these wide aerosol clouds play on the Earth climate is not yet clear and it has been even recently proposed that it might control inclusively the intensity of the cyclones reaching the American Continent[3].

Like for many other airborne particle sources, the Saharan episodes can be determined by their signature in terms of the ratios of concentration of elements obtained from the studies of several authors relative to which, Goudie [2] presents a review, pointing some differences between the Sahara aerosol having a direct path from the African Continent and that which has already crossed the European atmosphere.

In this work a time series of Saharan dust episodes is determined and the evolution of its composition along the 12 years of data available are reported and discussed.

MATERIAL AND METHODS

Airborne PM10 particles were collected in dual mode (PM2.5 or fine, and PM10-2.5 or coarse) in the Lisbon and vicinity area from January 1995 up to December 2006, using Gent samplers [4] or a home made (ITN) prototype sampler derived from the Gent samplers. Samples collected since 1995 up to 1998 were sampled at Faralhão, at about 40km South from Lisbon using a Gent sampler and a week base filter

replacement procedure described in detail in previous publications [5]. The ones collected from 1999 up to 2003 were sampled at the ITN Campus, in the North-East Lisbon outskirts, using a Gent sampler in a twice a week 24 hours continuous sampling methodology, also described in detail elsewhere [5]. Since January 2004, up to the present, samples have been collected at the ITN Campus using an ITN prototype sampler derived from the Gent sampler and using a weekly-based sampling methodology (the same as used at Faralhão from 1995 to 1998). A comparison between twice a week sampling procedures and the intermittent collection method, was previously made by Alves in 1998 [5] showing that apart from details, the two methods are essentially equivalent, the intermittent collection being potentially capable of a better full time representativity, at the same time as it allows for a reduction of number of collected samples.
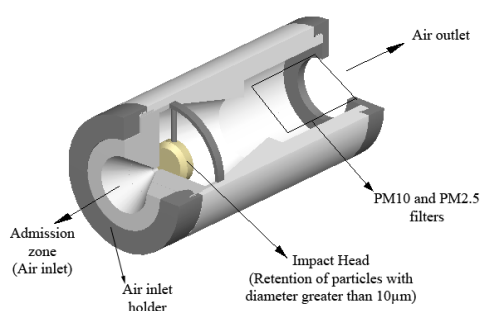

FIGURE 1. PM10 inlet of the ITN sampler evolution of the Gent sampler. The impact head is easily removed by unscrewing the Air inlet holder.

In what concerns the ITN design system, although essentially identical to the Gent samplers, it contains some improvement and small modifications, mainly in the PM10 head (see Fig. 1) which is designed to work at a 12 liters per minute sampling flow, thus providing a separation aerodynamic diameter closer to 2.5 ○m for the policarbonate Nuclepore® 8µm pore membrane filters used in the first stage of the NILU stacked filter units [6], than in the case of the Gent sampler at 17 liters per minute. Additionally, the PM10 separator impact plate is also easily removed from the separator head and the design was specially made to assure that a clean smooth surface impaction plate prepared in the laboratory is used in every sampling procedure. In fact, in the ITN prototype sampler, the whole PM10 head is prepared and opened within the laboratory facilities. The filter replacement carried out at the sampling site made by replacing the whole PM10 head, instead of

replacing just the stacked filter unit, as is frequent practice using Gent samplers.

In respect to filters, two stage NILU stacked filter unis were used loaded with 8µm pore in the first stage and 0.4µm pore in the second stage. All the filters were weighted, before and after sampling, on a 10 µg sensitivity balance up to 2000 and on a 0.1 µg sensitive micro-scale since then. After weighing, the filters were kept at -30ºC until they are prepared for PIXE analysis. Proton energy beams of 1.22 MeV and 2.12 MeV were used for determination of elements with $Z \leq 20$ (Ca) and $Z \geq 20$, respectively. All spectra were analysed using AXIL[7] and DATTPIXE [8] and results for Ca were compared for control purposes. Data obtained for the temporal series of PM2.5 and PM10-2.5 fraction was handled using the SYSTAT® v11 comercial code, to determine the correlation matrices for the elements concentrations temporal series containing more than 700 data points for: Al, Si, S, Cl, K, Ca, Ti, V, Mn, Fe, Ni, Cu, Zn e Pb, and without any prior standardization. SYSTAT® v11 was also further used to perform factor analysis on these data and identify the main sources present in the Lisbon and surrounding areas.

RESULTS AND DISCUSSION

TABLE 1: Factor loadings or composition in the correlation space for each of the 4 or 5 factors found in *1)*PM2.5 and *2)*PM10-2.5 data.

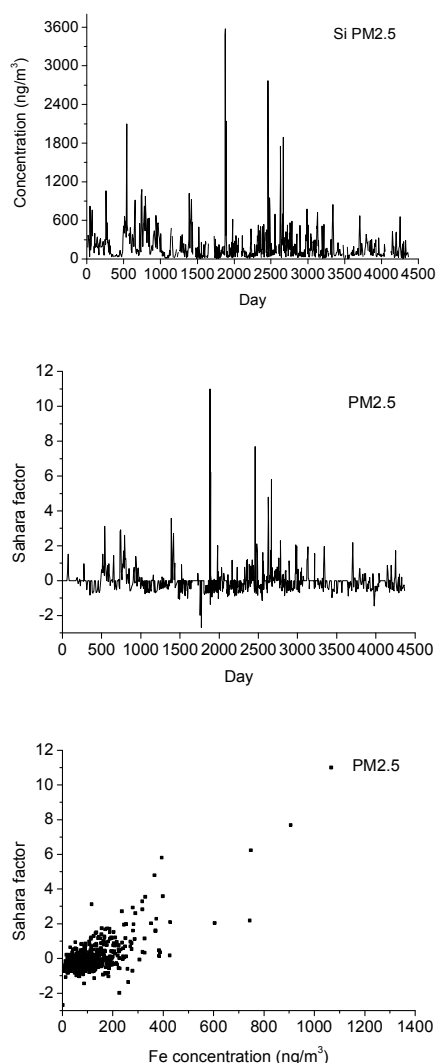|	*1a*	*1b*	*1c*	*1d*	*2a*	*2b*	*2c*	*2d*	*2e*
Al	0.9	0.1	0.0	-0.0	0.6	0.0	0.5	0.5	-0.1
Si	0.9	0.1	-0.0	0.0	0.7	0.0	0.4	0.5	-0.0
S	0.4	0.6	-0.1	0.0	0.2	0.2	0.7	0.2	0.3
Cl	-0.1	-0.2	0.1	0.6	-0.1	-0.2	0.8	-0.2	0.0
K	0.4	0.3	0.4	0.4	0.9	0.0	0.2	0.0	0.0
Ca	0.4	0.3	0.4	0.4	0.8	0.4	-0.0	-0.0	0.1
Ti	0.1	0.2	-0.2	0.7	0.9	0.2	-0.0	0.1	0.1
V	0.1	0.9	0.3	0.1	0.1	0.1	0.1	0.0	0.9
Mn	0.7	0.2	0.4	0.0	0.6	-0.1	-0.1	0.3	0.3
Fe	0.7	0.1	0.5	0.1	0.8	0.1	-0.0	0.3	0.2
Ni	0.2	0.8	0.4	0.0	0.2	0.5	0.0	0.0	0.7
Cu	0.1	0.1	0.8	0.1	0.2	0.1	-0.1	0.9	0.1
Zn	0.1	0.2	0.7	-0.0	0.1	0.8	-0.1	0.2	0.1
Pb	-0.1	0.5	0.4	-0.1	0.1	0.9	-0.0	-0.0	0.3

FIGURE 2. Time series for Si concentration and the Sahara factor from 1995 to 2006 and for the PM2.5 fractions. Day 0 is the 15th of January 1995. The correlation between these two time series is evident. In bottom the relation between the Sahara factor and the Fe concentration in the aerosol is clearly established.

The complete factor analysis of the PM2.5 and PM10-2.5 data yield four factors, for the PM2.5 data and five factors for the PM10-2.5 data.

Based on Nriagu [9] data and the factor loadings (or factors composition in the correlation space) presented in Table 1, the following interpretation was made for PM2.5 data: factor 1*a*) correlated to Al and Si was interpreted as a dust contribution, because the high peaks correspond mainly to Sahara events, this was named Sahara factor also because no scaling was applied before the PCA process, factor 1*b*) correlated

to S and V and Ni was interpreted as a fuel powered industries contribution, factor 1*c*) related to Cu and Zn was interpreted a general industry contribution, mainly coal powered, and finally, the factor 1*d*) related to chlorine was just named chlorine factor and is discussed elsewhere [10]. In the case of coarse particle data also presented in Table 1, the following interpretation was made: factor 2*a*) correlated to K, Ti, Ca and Fe was interpreted as dust contribution, and named Sahara like in the case of the fine particles, factor 2*b*) correlated to Ni, Zn and Pb was interpreted as a cement industry contribution, 2*c*) related to Cl and S was interpreted as a sea salt contribution, 2*d)* related to Cu corresponds to a mine exploitation contribution,
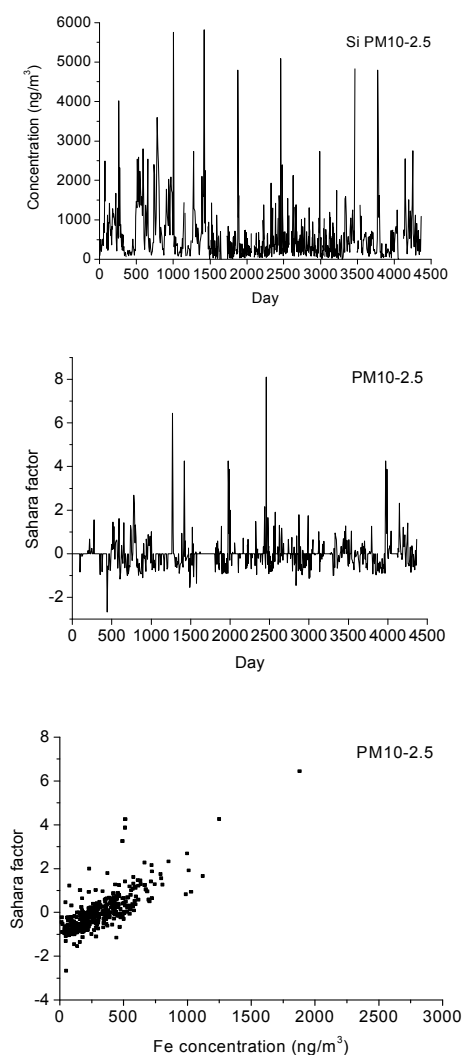

FIGURE 3 Time series for Sahara factor from 1995 to 2006 and for the PM10-2.5 fractions. Day 0 is the 15th of January 1995. The correlation between these two time series is not so

evident. In bottom the relation between the Sahara factor and the Fe concentration in the aerosol is clearly established.
and finally, the factor 2*e*) correlated to V and Ni was interpreted as a fuel powered industries contribution.

In Fig. 2 and 3 the time sequence of Sahara events is compared to the Si concentrations and the intensity of the Saharan factor compared to the determined Fe concentration. It can be concluded that Saharan dust episodes do carry much iron. In Fig. 4 the annual correlation between Fe and V is presented. The Saharan aerosol composition is therefore not stable during the whole 12 years but suffers periodic contamination, as can be concluded by the periodic like behaviour of the V-Fe Pearson correlation coefficient. This contamination will therefore also necessarily impact on all the ecosystems where the dust falls.
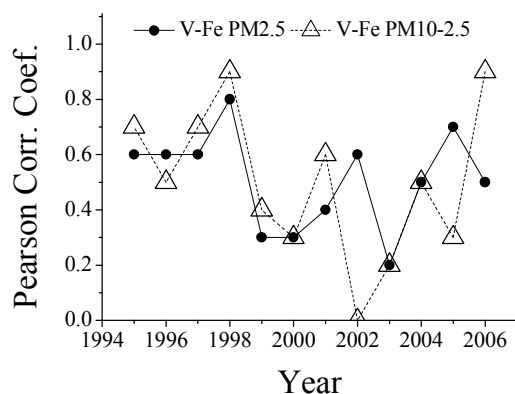

FIGURE 4. Pearson correlations coefficient for V-Fe for both the PM2.5 and PM10-2.5 fractions. Day 0 is the 15th of January 1995. The correlation between these data is clear.

CONCLUSIONS

A 12 year time series of aerosol data was compiled and dealt with using factor analysis. One of the factors determined is attributed to Sahara dust. Calculations made on the ratio of Si to Fe concentration for both PM2.5 and PM10 provide a ratio compatible to the values presented by Goudie [2] for the composition of direct African dust. Still, the correlation between Fe and V, showing a periodic like nature take us to believe that natural fluctuations on atmospheric paths have important influence on the composition of the Sahara dust aerosol carring Fe on to the Atlantic Ocean. This result if possible to confirm by other means, might call the attention to possible periodic contamination events of the ocean ecosystem.

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