CHARACTERIZATION OF ATMOSPHERIC AEROSOLS IN GRAN CANARIA (CANARY ISLANDS, SPAIN)

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ABSTRACT

Atmospheric aerosols originate from both natural and anthropogenic sources. Measurements of aerosol concentration and their composition can help to characterise important sources of aerosols in different regions and determining air quality Atmospheric loading were obtained in different sampling locations in Gran Canaria (Canary Islands) to know the spatial and seasonal distribution of Saharan inputs in Canary region. One of the objectives proposed were to evaluate the anthropogenic contribution in the atmospheric samples.

Aerosol samples were collected using glass fiber and cellulose filters. The 30% of filters were subjected to acid digestion. Dust concentration in the air were measured using a High Volume Capture System (CAV-A) of MCV, S.A. equipped with a rectangular head made of PVC.

Metals were analysed by the Atomic Absorption and electrochemical methods. Crustal (Fe, Mn, Ti and Co) and non-crustal (Cu, Cr) trace metals were analysed. Selected samples were chosen in function of representative periods of the year and different atmospheric loads. They were classified depending on the air masses trajectories and seasons. Relationships between metal concentration of the dust and its origin have been worked out. Air trajectories and satellite image have been used to trace Saharan dust origin. Relationships between the dust concentrations of the crustal elements (Ti, Co, Mn and Fe) and the atmospheric loading have been found. Other elements, such as Cu or Cr, do not show any correlation with atmospheric loading.

1. INTRODUCTION

The atmosphere is the dominant pathway by which both natural and pollutant materials are transported from continents to the oceans. These substances include mineral dust, nitrogen species from combustion processes and fertilisers and a wide range of synthetic organic compounds from industrial and domestic sources. Trace metals in the atmosphere are associated with aerosol particles that are produced both naturally and as a result of anthropogenic activities.

The present study focuses in mineral dust and the heavy metals contribution proceeding from atmospheric natural and anthropogenic sources. Atmospheric transport of mineral aerosol from continental sources could have an essential impact on the global climate variability[11].

The influence of mineral dust in the atmosphere has been observed at many geographical regions. In particular, arid regions such as the Sahara Desert, and semiarid regions, such as North Africa or Sahel, are susceptible to the mobilization of dust particles which are then transported within the NE trade winds system over the Atlantic Ocean for long distances[1,2,3]. Many authors have shown that large amounts of soil dust are mobilized by winds and that substantial quantities can be carried great distances such as Sargasso Sea[4]. Saharan atmospheric pulses appear like intermittent increases in concentrations within the average loading concentration of the atmosphere.

Atmospheric transport and deposition processes are highly episodic, related to emission patterns and meteorological conditions [8], with a clear annual cycle with maximum dust concentrations in the summer and a winter minimum in Bermuda and Barbados. However, in Canary Islands region does not appear to present this marked variability[5,6].

Aluminium, titanium and manganese are primarily crustal in origin, entering the atmosphere during weathering of soils. Aluminium accounts for ~8.4% of the continental crust. titanium ~0.4% and manganese ~0.14% [9]. Release of manganese during smelting and use of some organic compounds (methylcyclopentadienyl manganese tricarbonyl) as an octane enhancer in unleaded vehicle fuels in some countries may partially account for enhanced levels of fine-mode aerosol manganese seen in polluted air [10]. Iron is related with mineral dust and accounts for 3.6% in crustal material. Eolian deposition supply Fe in oligotrophic areas where this element control the primary production[12].

Other elements, like Pb, Cr and Cu, is related with the high-temperature anthropogenic processes in the northern hemisphere[13].

The present study focuses on the interannual and seasonal variability of dust loadings in the Canary Islands during a sampling period of two years. Proposed objective was to evaluate the metal content of atmospheric samples in different periods to classify the samples using metallic indicators (crustal and/or anthropogenic origin) in analysed samples.

2. MATERIAL AND METHODS

2.1. Sampling stations and collection

Dust concentrations in the air were measured by using five high-volume capture systems (CAV-A) from MCV, S.A., equipped with a rectangular filter heads made of PVC. The device was operated for 12 hours daily using a flow rate of 60 m^3/h. The samples were taken daily during period of 1997 and 1998 at "Pico de la Gorra" at the top of Gran Canaria Island (1980 m) and Tafira. Glass fiber 20 x 25 cm (Whatman GF/A) and Whatman 41 filters were used to collect the material (Figure 1). Hydroscopic effects were not observed in Whatman GF/A. Aerosol concentration was obtained by the difference of weight between the dried filters (80°C during 12-24 h) before and after the collection. Replicate samples were collected simultaneously, with different

collection equipment having cumulative errors less than 5%. Blanks of filters were used to determinate the precision of the method (L.D. 3 $\mu g \cdot m^{-3}$ with a S.D. of 1.4%). Approximately, ¼ of each fiter was used for the trace metal analysis.

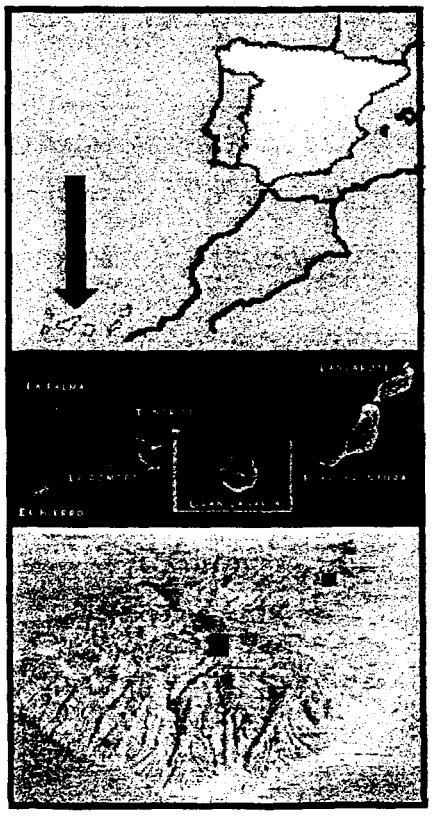

Figure 1. Location of sampling places in Gran Canaria island (Canary Islands).

2.2. Chemical analysis

Analyses of Fe, Mn, Ti, Co, Cr and Cu in particles were carried out after total digestion with HF, HNO_3 and $HClO_4$ in PTFE beakers [7]. The digested samples were diluted to volume by double-distilled water. Metal concentrations were measured on a Varian Graphite Furnace Atomic Absorption Spectrometer (GFAAS). Metal calibration analyses was performed by standard additions. Triplicate measurements were performed, and the reproducibility was found to be between 0.9 and 3.1 % for all the metals analysed.

Different blank filters were exposed in the sampling location (without filtration) to evaluate the contribution of samplers, manipulation and filter composition in metal contribution in the samples. Trace metal concentrations do not present important variations (Co, 3.5%; Cr, 1.5%; Cu, 6.4%; Fe, 8.9%; Mn, 13%; Ti, 9.0%) independently

of exposed days. In the same way, this variation was similar than replicate analysis of non-exposed filters.

Digestion validation was evaluated on the basis of analyses of International Standard Reference materials: MESS-2 of National Council of Canada. All elemental results were within 10% of the certified values (Table 1).

Element	This study (ppm)	Certified values (ppm) of MESS-2
Al	160.97 ± 8.40	162.00 ± 4.90
Co	11.98 ± 2.40	13.80 ± 1.40
Cr		106.00 ± 8.00
Cu	31.40 ± 1.10	39.30 ± 2.00
Fe	52.63 ± 2.07	62.20 ± 3.10
Mn	329.90 ± 16	365.00 ± 21.00
Ti	----------	----------

Table 1.

Analysis replicates of six portions of yielded precision <12 %, which show that the collected aerosol material is evenly distributed across the filter (Table 2).

Selected samples to measure the atmospheric composition have been chosen along the year between dust outbreaks (with brown colour and dust loading greater than 50 $\mu g \cdot m^{-3}$) and clean periods (without colour and dust loading less than 20 $\mu g \cdot m^{-3}$) in 30% of collected samples during 1997-1998 period. Figure 2 shows the dust concentration variability during the dust collection and the read squares indicate the digested samples.

Element	Concentration	% Error
Al	110.6 ± 13.6 mg Al/g	12.3
Co	14.6 ± 2.5 µg Co/g	3.5
Cr	123.6 ± 14.2 µg Cr/g	11.5
Cu	36.2 ± 2.0 µg Cu/g	5.6
Fe	33.3 ± 3.2 µg Fe/g	9.6
Mn	158 ± 20.3 µg Mn/g	11.8
Ti	4.5 ± 0.1 mg Ti/g	2.6

Table 2.

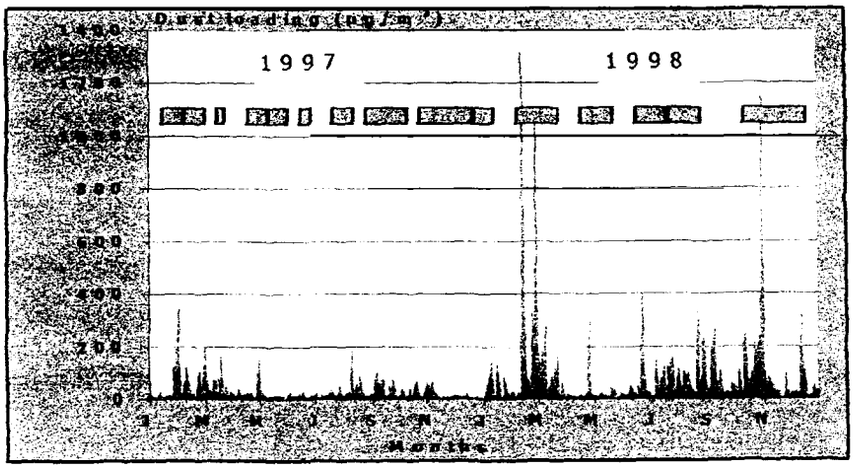

Figure 2. Dust loading (in µg·m-3) variability during 1997-1998 period in Gran Canaria island (Canary Islands).

3. RESULTS AND DISCUSSION

We present the results of daily concentrations of mineral dust in air during the 1997-1998 period in Pico de La Gorra. These events, in the form of "pulses", lasted an average of 3 to 8 days (Figure 3). During the sampling, the highest values of dust concentration have been measured in winter. Average annual concentrations were quite different between them: 27 $\mu g \cdot m^{-3}$ in 1997 and 70 $\mu g \cdot m^{-3}$ in 1998. These differences are observed in Saharan dust days: during 1997, a maximum concentration of dust was 340 $\mu g \cdot m^{-3}$, although a maximum of 1300 $\mu g \cdot m^{-3}$ was obtained in 1998. These differences are a good indicator of the strong annual variability experienced during the sampling period.

We have classified the sampling in terms of "clean days" and "Saharan days", according to the dust concentration in the atmosphere. We chose the dust concentration higher than 100 $\mu g \cdot m^{-3}$ to distinguish the Saharan outbreak periods. The variability of dust concentration in the air during "non-Saharan days" is quite low, whilst it is much higher during "Saharan days". Table 3 present average values of atmospheric inputs in different locations of Gran Canaria island.

SAMPLING YEAR	NON-SAHARAN DAYS	SAHARAN DAYS
1994 (Tafira)	37.8 ± 15.0	171.6 ± 43.9
1995 (Tafira)	34.1 ± 13.3	186.1 ± 110.5
1997 (Pico La Gorra)	18.6 ± 12.7	126.3 ± 54.2
1998 (Pico La Gorra)	21.2 ± 13.7	199.3 ±209.1

Table 3. Average mineral aerosol (in $\mu g \cdot m^{-3}$) in the studied period.

Seasonal distributions (Figure 4) indicate that the highest frequency of Saharan dust inputs in the Canary Islands is produced during winter (42%) and summer (29%). These events decrease during spring (6%).

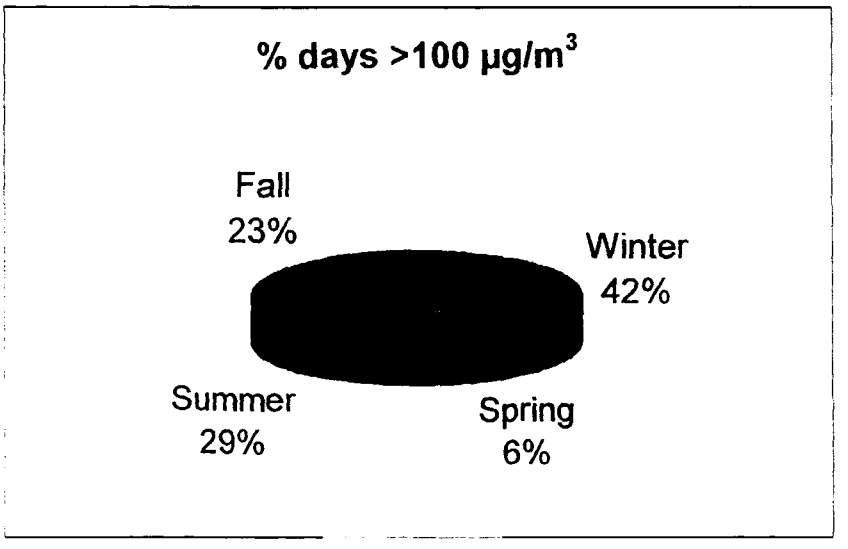

Figure 4. Seasonal distribution of Saharan dust inputs obtained of dust loading data during 1997-1998 period.

Initially, samples selection for digestion was made in function of dust loading data (in $\mu g \cdot m^{-3}$). Afterwards, we use the trajectory maps of air masses supplied by Ratmeyer (personal communication). To perform the obtained results, we made a simple classification in function of air mass trajectory, air mass direction (north, south, east, west) and seasons (winter, spring, summer autumn). With this preliminary classification, we want to show relationships between metal concentration in the air and some of these variables.

The sources for atmospheric trace elements frequently are investigated through the analysis of elemental concentration ratios. One approach for this is to compare the elemental ratios in the samples with those in a likely source material, and this is done by calculating Enrichment Factor (EF). Enrichment Factors (EF) in the dust are calculated as:

$$EF = (X/Ref)_{sample}/(X/Ref)_{crustal}$$

where (X/Ref) is the concentration ratio of the element of interest to that of a reference element, and the susbscript "sample" and "crustal" refer to the compositions of the sample and the source material of interest. EF values less than 10 can infer that the source dominates the concentration of the element in the sample. EF values greater than 10 are considered that a significant fraction of the element have a non-crustal origin.

Exposed data are related to 1997 in Pico de La Gorra. Using Ti as crustal reference element, EF_{Fe}, EF_{Mn} and EF_{Co} are less than 10 for 90% of the analysed samples. EF_{Cr} range betweeen 1 and 600 and EF_{Cu} vary between 1 and 200. These values could confirm the different origin of the samples.

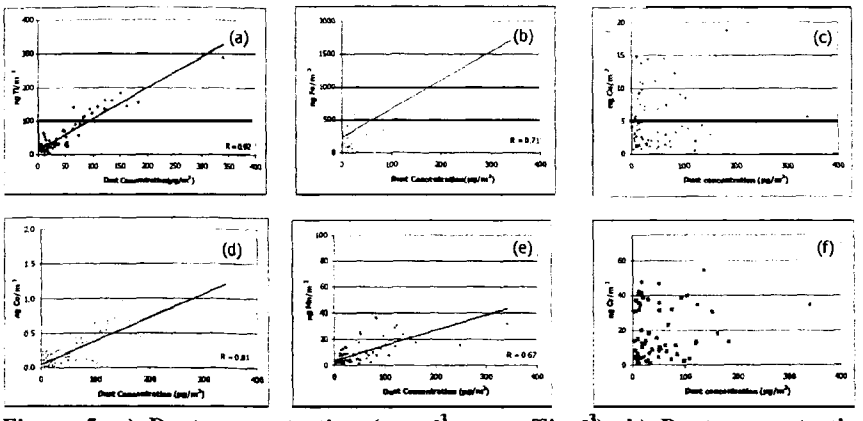

Figure 5. a) Dust concentration ($\mu g \cdot m^{-3}$ vs ng $Ti \cdot m^{-3}$); b) Dust concentration ($\mu g \cdot m^{-3}$ vs ng $Fe \cdot m^{-3}$; c) Dust concentration ($\mu g \cdot m^{-3}$) vs ng $Cu \cdot m^{-3}$; d) Dust concentration ($\mu g \cdot m^{-3}$ vs ng $Co \cdot m^{-3}$); e) Dust concentration ($\mu g \cdot m^{-3}$ vs ng $Mn \cdot m^{-3}$); f) Dust concentration ($\mu g \cdot m^{-3}$ vs ng $Cr \cdot m^{-3}$)

In other hand, figure 5 show the relationship between the atmospheric concentration of lithogenic metals (a, b, d, e) in the dust ($ng \cdot m^{-3}$) and the dust concentration in the air ($\mu g \cdot m^{-3}$). The distribution patterns fit into a linear correlation for these elements, especially for Ti. Relationship between the atmospheric concentration of non-crustal metals (c, f) does not show a lincar regression. Ti and Co concentrations in atmospheric dust show a small variability during the year (3.8 ± 1.9 $mgTi \cdot g^{-1}$; 10.8 ± 5.2 μg $Co \cdot g^{-1}$, respectively). However, Mn and Fe show a large variations with coupled maximum. As an example, Fig. 6 shows the annual Fe distribution by trajectories. Samples from north show an Fe maximum in spring. Samples from south do not show important changes in Fe concentrations. In east samples, Fe shows a maximum in fall. Finally, samples from west shows a maximum in spring and fall.

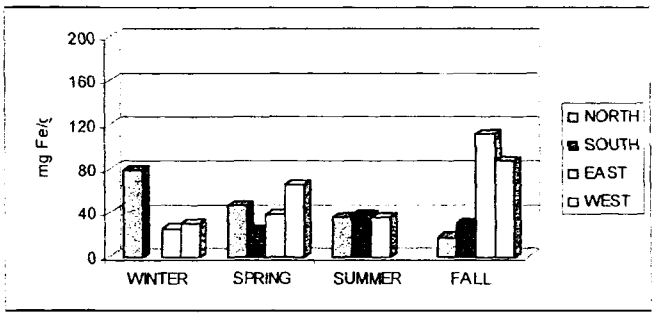

Figure 6. Annual Fe distribution by trajectories.

Changes of Fe percentages in the mineral dust could be related with the origin of sampling dust. As an example, figure 7 show different origins: from north-east (a) low % of Fe and from south-east (b) higher % of Fe.

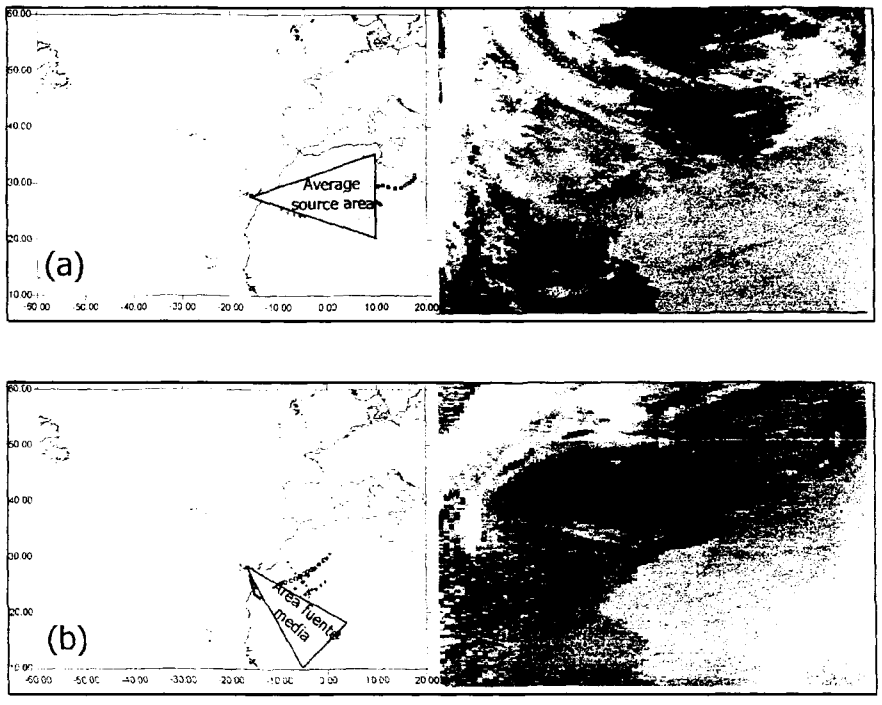

Figure 7. Origin of sampling dust according to Fe content.

CONCLUSIONS

We can conclude that Saharan dust inputs in Canary Region are produced during winter and summer periods. These events lasted an average of 3 to 8 days in accordance with experimental data, that the seasonal distribution of Saharan dust inputs seems to repeat in both sampling years in Pico de La Gorra. Principal difference between both year is that, during 1998 summer, Saharan dust events were higher than 1997. It exists, therefore, a strong interannual and seasonal components that control the Saharan dust inputs to the Canary region which could be related with NAO (North Atlantic Oscillation) variations.

With respect metal content, Ti, Mn, Fe and Co have a lithogenic origin according to Enrichment Factors. However, Cr and Cu do not present linear correlation with dust loading. For that, we could these elements have a different origin.

Differences in iron content in Saharan dust inputs could indicate a different origin of the atmospheric dust which arrive the Canary Region.

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