Transport of North African industrial pollutants mixed with desert dust in the Saharan Air Layer

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Abstract — **Chemical composition of TSP, PM_{10} and $PM_{2.5}$ during Saharan dust events in North Atlantic free troposphere was studied. Samples were collected from 2002 to 2008 at Izaña Global Atmospheric Watch observatory, placed a 2367 masl in Tenerife (Canary Islands). During non Saharan dust events concentrations of all PM components and bulk PM levels are low due to the clean air conditions in the free troposphere (mostly < 2 µg/m^3). Species potentially linked to anthropogenic emissions, such as sulphate, nitrate, ammonium and some trace elements/metals (Pb, V, Ni), are detected within the Saharan Air Layer (SAL) mixed with desert dust. In order to identify the source region of dust and pollutants, data were analysed with Median Concentrations At Receptor (MCAR) plots. The southern slope of Atlas mounts emerge as the most frequent source of the soil desert dust. Industrial emissions occurring along the Atlantic coast of Morocco, Northern Algeria, Eastern Algeria and Tunisia appear as the most important source of the nitrate, ammonium and a fraction of sulphate observed in the SAL. These emissions are mostly related to crude oil refineries, phosphate-based fertilizer industry and power plants. Although desert dust emissions appear as the most frequent source of the phosphorous observed in the SAL, high P concentrations are observed when the SAL is affected by emissions from open mines of phosphate and phosphate based fertilizer industry. The results also show that a significant fraction of the sulphate observed in the SAL is linked to soil emissions of evaporite minerals in well defined regions where dry saline lakes (chotts) are present. These interpretations of the MCAR plots are consistent with the results obtained with the Positive Matrix Factorization receptor modelling. The results of this study show that North African industrial pollutants may be mixed with desert dust and exported in the SAL.**

Keywords— **Saharan Air Layer, mineral desert dust, sulphate, nitrate, industrial pollutants, air quality, refinery, fertilizers phosphate industry.**

I. Introduction

Desert regions of Northern Africa are the largest source of soil dust suspended in the atmosphere of the Earth. It is estimated that annual emissions range within the interval 300 - 1600 Tg/y. They account for 60-70% of global desert dust emissions and they are 2 -3 times larger than those of the Asian deserts, the second most important dust source region (Engelstaedter et al., 2006).

Dust plays an important role in processes affecting climate, biogeochemistry and air quality. Moreover, in urban areas affected by advections of Saharan dust, an increase in mortality (Pérez et al., 2008; Jiménez et al., 2010) and in cardiovascular diseases (Middelton et al. 2008) has been observed.

Regional dust production and exportation in North Africa experience a marked seasonal evolution. Because of the seasonal shift of the intertropical convergence zone, the sources of soil desert dust located in Sahel are mostly activated in winter (Harmattan winds), whereas those located in northern subtropical Saharan latitudes are activated in summer (Engelstaedter et al., 2006). Thus, the so-called Saharan Air Layer (SAL) is westward exported at low "tropical" latitudes (<15ºN) in winter and at higher "subtropical" latitudes in summer (15 – 30 ºN). This behavior can be observed in Figure 1, where the Aerosol Index (AI) averaged for January and July is shown.

Although soil dust emissions are, by far, the most important source of the particles present in the SAL, there is an increasing number of evidences pointing that anthropogenic activity may be prompting changes in the amount and composition of the particles present in the SAL. Three examples:

• Dust particles exported in the winter tropical SAL (Figure 1B) are often externally mixed with carbonaceous and inorganic trace species (e.g. K+) linked to biomass burning in Sahel during the dry season (Formenti et al., 2003; Capes et al., 2008).

• A number of observations have shown that soil dust in the SAL is very often mixed with sulphate and nitrate; e.g. observations in the Canary Islands, Cape Verde and Caribbean (see review in Rodríguez et al., 2011). The few studies focused on investigating the origin of these pollutants have

shown that the transport of pollutants from Europe and their mixing with North African desert dust may contribute to the observed dust – pollutants mixing (Millán et al., 1997; Gangoiti et al., 2006, among other).

• There are huge uncertainties on how human activities are changing soil dust emissions. Zender et al. (2004) defined anthropogenic soil dust as that part of the dust load that is produced by human activity. This may occur by two ways: 1) by land use which changes soil surface conditions that modify the potential for soil dust emission (e.g. by agriculture, mining, livestock, vehicles or water management), and 2) by modifying climate, which in turn modifies dust emissions, for example, by changes in surface winds or vegetation growth.

The objective of this study is to investigate the origin of some aerosol species observed in the SAL that may be influenced by anthropogenic activities. We focus part of our attention on nitrate, ammonium and sulphate. The mixing of these species with dust may prompt changes in the physical properties of the SAL and this may have important consequences in processes affecting climate. For example, the coating of the dust particles with these species may enhance the hygroscopic properties and light scattering efficiency of the SAL particles.

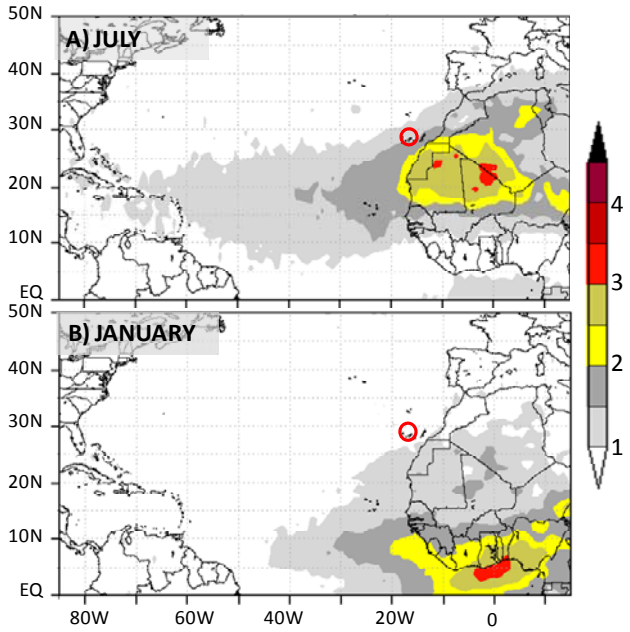

Fig 1 Average Aerosol Index in July and January. Red circle highlights the location of Izaña.

II. METHODOLOGY

A. Sampling site

Measurements and sampling were performed at the Izaña "Global Atmospheric Watch" (GAW) observatory (16º 29' 58'' W; 28º 18' 32'' N; http://www.aemet.izana.org). This is a free troposphere site located in Tenerife (Canary Islands) at 2367 meters above sea level (ma.s.l), above the mantle of stratocumulus typically present on the top of the marine boundary layer. Izaña remains within the SAL during most of summertime (its location is highlighted with red circle in Figure 1).

B. Size distribution and particulate matter sampling

Samples of TSP, PM_{10} $PM_{2.5}$ are systematically collected at Izaña. The PM_x monitoring program was based on TSP and $PM_{2.5}$ from May 2002 to December 2004, on PM_{10} and $PM_{2.5}$ since 2005. Simultaneous TSP, PM_{10} and $PM_{2.5}$ sampling is performed every summer since 2008. PM_x concentrations were determined by gravimetry after condition to 20ºC of T and 30-35 % RH. Sampling was performed on micro-quartz fibber filters.

Particle size distribution was measured with an Aerodynamic Particle Sizer (APS; TSI™) and with a Scanning Mobility Particle Sizer (SMPS; TSI™).

B. Chemical characterization

Filters were analyzed by different techniques in order to determine the concentrations of about 60 elements and components. A half of the filter was bulk acidic digested (HF:HClO4:HNO3), and the solution obtained was analysed with ICP-AES and ICP-MS. A quarter of the filter was water leached for the determination of the concentrations of soluble ions by means of Ionic Chromatography HPLC, for Cl^-, SO_4^{2-} and NO_3^-, and ion selective electrode for NH_4^+. Relative errors of have been estimated as < 10%. Total carbon (TC) concentrations were measured by using an Elemental Carbon Analyser (LECO). Levels of organic and elemental carbon (OC and EC) were determined by thermal-optical transmission technique using a Sunset Laboratory OC-EC analyser

C. Source regions of dust and other aerosol species

The potential source regions of dust and of other aerosol species (e.g. sulphate or nitrate) were identified by analyzing the "Median Concentrations At Receptor (MCAR)" plots determined for each aerosol species analyzed at Izaña. These MCAR plots represent the median concentrations, recorded at Izaña, of a given aerosol compound when air masses passed above each 1ºx1º degree pixel shown in the

lat x lon grid.; e.g. Figure 6A shows the MCAR map for nitrate. MCAR plots were determined using five days back-trajectories calculated at 00:00 UTC using the HYSPLIT software (Draxler and Rolph, 2010) and 50km x 50km ECMWF data.

D. Sources of information

MCAR plots were interpreted using a wide variety of sources. The location and nature of mining and industrial activities were identified using the Mineral Yearbooks of the US Geological Survey (Newman, 2008; Taib, 2008a; 2008b) and online information on power plants, refineries and chemical plants. Figure 2 shows the location of the industrial sources of pollutants identified in North Africa. The coordinates of the identified sources of dust and other aerosols is provided in order the reader may use Google Earth ™ and Google Map ™ for having a satellite view.

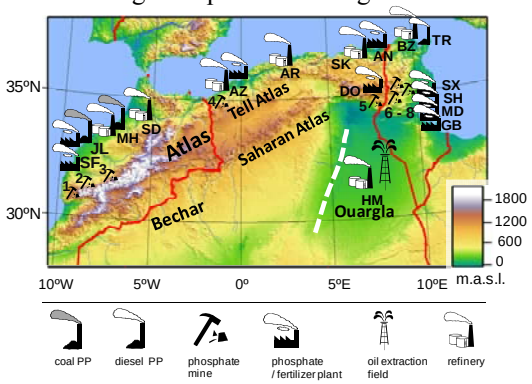

Fig 2 Location of the main industrial states in Morocco, Algeria and Tunisia

III. RESULTS AND DISCUSSION

A. Particulate matter composition

Table 1 shows the mean composition of PM_{10} during events in which this parameters showed bulk mass concentration data within the percentile intervals 1 – 10th, 55 – 85 th and 85 – 99th, representative of clean free troposphere, moderate dust events and intense dust conditions, respectively. The increase in dust concentrations throughout the sequence clean free troposphere, moderate dust and intense dust conditions (e.g. ~ 0.4, 19 and 70 µg/m^3 of dust in PM_{10}) is associated with an increase in the absolute concentrations of sulphate (e.g. ~ 0.3, 1.2 and 2.4 µg/m^3), nitrate (e.g. ~ 0.1, 0.6 and 1.2 µg/m^3) and ammonium (e.g. 0.06, 0.1 and 0.3 µg/m^3), although a decrease in their relative contribution (%) to PMx is observed. During dust events, sulphate, nitrate and ammonium accounted for 2 - 6%, 1 - 2% and 0.1 - 0.6% of bulk PMx, respectively.

Sulphate and nitrate exhibited low concentrations under clean free troposphere conditions and high levels during dust events. Ammonium-sulphate salt only accounts for about 20-36% of $SO_4^=$ in TSP, for 28-30% of $SO_4^=$ in PM_{10} and for 37-56% $SO_4^=$ in $PM_{2.5}$ during dust events

Table 1. Mean composition of PM_{10} averaged in three intervals of PM levels: 1th -10th, 55th – 80th and 85th – 99th. Und: undetermined (difference between bulk PMx concentrations and the difference of the sum of the determined compounds). Σ: sum of the determined chemical compounds.

	1th	10th	55th	80th	85th	99th
Al:	0	0	0.6	3.9	5.1	11.7
	µg/m^3	**%**	**µg/m^3**	**%**	**µg/m^3**	**%**
N	22		51		28	
PM_{10}	2.96		29.29		100.87	
und	0.59		5.28		23.28	
Σ	2.37	80	24.01	82	77.59	76.9
dust	0.39	13.1	19.24	65.7	69.93	69.3
$SO_4^=$	0.26	8.7	1.15	3.9	2.42	2.4
NO_3^-	0.09	2.9	0.61	2.1	1.18	1.2
NH_4^+	0.06	2.1	0.13	0.5	0.26	0.3
OM+EC	1.57	53.1	2.88	9.8	3.81	3.8

B. Size distributions

Volume size distributions measured during dust episodes shows a bimodal size distribution (Figure 3), centred at 240 nm and 3.0 µm. The fine mode is attributed to the presence of ammonium sulphate, whereas the coarse mode is predominantly due to dust.

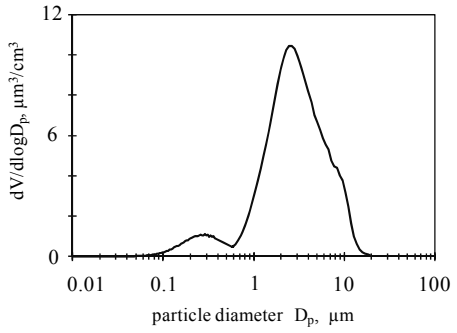

Fig 3 Mean particle volume size distribution during dust events

C. Transport pathways of Saharan airflows

The frequency by which air masses passed over each 1º x1º pixel included in the MCAR plot is shown in Figure 4. The region of high frequency (≥ 50 counts) reveals that there is a well defined transport pathway (red arrow in Figure 6B): air original from the Mediterranean flows North to South across Tunisia and Northern Algeria and is then westward transported along the Southern slope of the Atlas mounts toward the North Atlantic Ocean. This transport pathway is similar to the "mean airflows" previously described by Millán et al. (1997) and Gangoiti et al. (2006). Air from other regions out of the main transport pathway may also be transported to Izaña and mixed with the SAL.

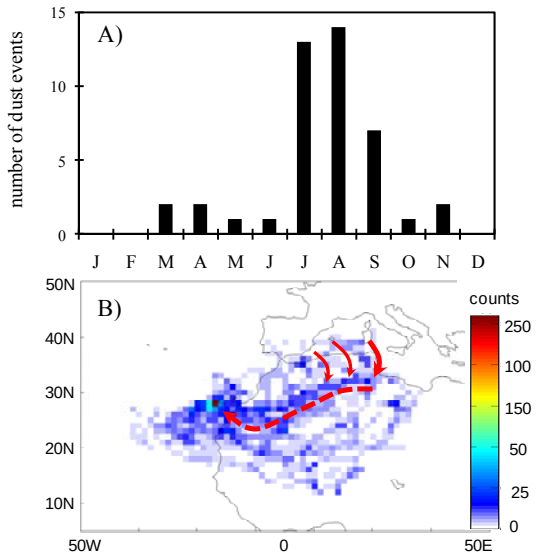

Fig 4 Number of events with dust concentrations > 10 $\mu g/m^3$ in PM_{10} (A) and frequency of pass of trajectories by each 1ºx1º pixel (B)

D. Sources of dust

The objective of this section is to identify location of the main sources of the soil dust and to highlight the different geographical distribution with respect to the industrial sources that will be described below. Figure 5 shows the MCAR plot of Al at Izaña. High concentrations of Al are observed when air masses have flowed over: Bechar basin (Western Algeria), Northern Algeria - Tunisia, and Ouargla basin (Eastern Algeria). All these regions are topographic lows where alluvial deposits are accumulated. A detailed description of the features of the observed soil dust sources is out of the scope of this paper. Details on the environmental features of these dust source regions are presented by Rodríguez et al. (2011).

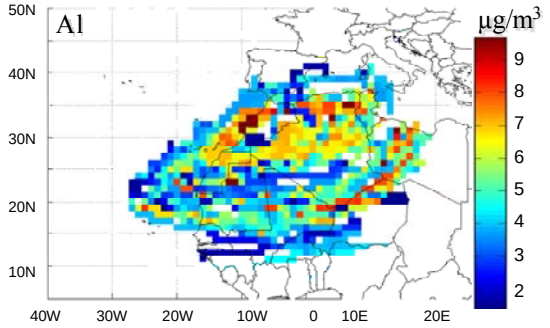

Fig 5 MCAR plot for Al recorded at Izaña

E. Nitrate, ammonium and sulphate: role of industrial emissions

Figure 6 shows the MCAR plots for NO_3^- and NH_4^+. High concentrations of these aerosol components are recorded when air arriving to Izaña have flown over the Atlantic coast of Morocco, Eastern Algeria and Northern Algeria and Tunisia. The following industrial states, emission sources of gaseous precursors (SOx, NOx and NH_3) of these aerosol compounds, have been indentified in these regions (Figure 2):

- Morocco. A region of high concentrations of nitrate, sulphate and ammonium (2.0 – 2.2, ~ 0.12 and 3.0 – 3.5 $\mu g/m^3$, respectively) is observed (in the MCAR plots) parallel to the Atlantic coast of the country. The following industrial states are placed, North to South, in this region:
  - Sidi Kassem (34.233ºN, 5.718ºW), a crude oil refinery with about ~30,000 barrels per day (bpd) production,
  - Great Casablanca area, where Mohammedia crude oil refinery (33.686ºN, 7.426ºW; ~125,000 bpd) and several power stations are located. About half of the SO_2 and NOx emissions have been attributed to Mohammedia coal fired power station (33.682ºN, 7.434ºW; 600Mw),
  - Jorf Lasfar, where the largest coal fired power station of the country is placed (33.105ºN, 8.637ºW; 1,400Mw),
  - Jorf Lasfer (33.111ºN, 8.606ºW) and Safi (32.222ºN, 9.249ºW), where two large chemical plants that produce phosphoric acid and ammonium phosphate (as part of fertilizer industry) are placed.

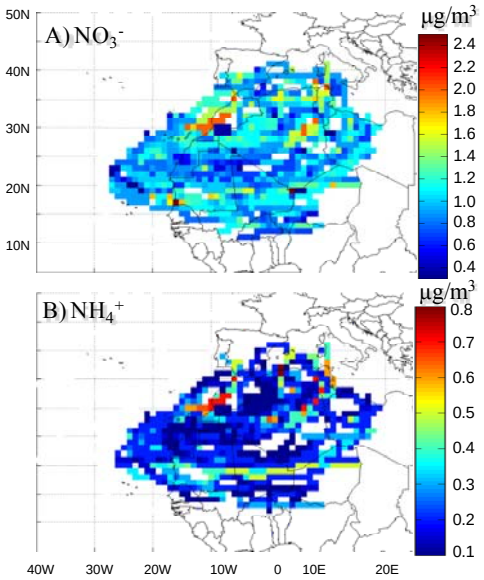

Fig 6 MCAR plot for nitrate and ammonium at Izaña

- Eastern Algeria. High concentrations of nitrate, sulphate and ammonium (1.5 – 2.0, 2.5 – 3.5 and 0.3 – 0.6 µg/m^3, respectively) are observed in Ouargla region. This area is centered over Hassi Messahoud (31.670ºN, 6.070ºE), where one of the largest oil extraction field in Africa and two crude oil refineries (30,000 bpd) are placed.
- Northern Algeria and Tunisia. High nitrate, sulphate and ammonium concentrations are also observed in the coast of Algeria and Tunisia, in the Mediterranean, where the following industrial facilities are placed:
  - Arzew crude oil refinery (60,000 bpd),
  - Algier crude oil refinery (60,000 bpd),
  - Skikda (36.879ºN, 6.945ºE) crude oil refinery (300,000 bpd),
  - Annaba (36.871ºN, 7.765ºE) petrochemical plant for the production of sulphuric acid, phosphoric acid and diamonium phosphate,
  - Bizerte (36.800ºN, 10.290ºE) crude refinery (35,000 bpd),
  - Rades (36.799ºN, 10.286ºE) power plant,

V. Summary and Conclusions

Particulate matter samples (TSP, PM_{10} and $PM_{2.5}$) representative of the northern side of the summer Saharan Air Layer (SAL) were collected in the North Atlantic free troposphere at Izaña Global Atmospheric Watch observatory (Tenerife, Canary Islands). An analysis of the chemical composition of these PMx samples shows that soil desert dust is very frequently mixed with particulate pollutants. The results of this study evidence that:

• The areas located at the south of the Southern slope of Atlas mounts are a significant source of soil dust advected toward the Atlantic in summer in the northern edge of the Saharan Air Layer.

• Emissions of the crude oil refineries, "phosphate based fertilizer industry" and power plants, located in the Atlantic coast of Morocco, Northern Algeria, Easter Algeria and Tunisia, significantly contribute to mix desert dust with particulate pollutants such as nitrate, sulphate and ammonium. The chemical composition of PMx and the size distribution data suggest that both internal and external mixing may occur in the aerosol population present in the SAL.

More investigations are needed for having a comprehensive view of the processes involved in the desert dust and pollutants mixings, and their implications on the physico-chemical properties of the SAL. Studies performed by Millán et al. (1997) and Gangoiti et al. (2006) showed that aged pollutants emitted in Eastern Spain and re-circulated in the Western Mediterranean basin may also be mixed with North African desert dust, and then be exported to the North Atlantic in the SAL. These coastal and mountain breezes involved in the regional transport and aging of pollutants have also been described for the North African side of the Western Mediterranean (Algeria – Tunisia; Bouchlaghem et al., 2007). Southward transport of particulate pollutants from urban coastal areas of Algeria to Saharan inner sites (across Atlas) was also described by Yassaa et al. (2001).

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