Individual particle analysis of atmospheric aerosols from Pico mountain, Azores

B.J. Vieira[1,2], M.C. Freitas[2], H. Th. Wolterbeek[1]

Abstract — PICO-NARE observatory is an experimental site on Pico mountain summit (38,47ºN, 28,40ºW, 2225m altitude) in Pico Island, Azores, Portugal, where air masses from surrounding continents (Africa, Europe, Central North Atlantic and North America) carrying aerosols from anthropogenic and/or natural emissions, pass through. Aerosol composition measurements in Pico on some events of 2005 and backward trajectories of particularly trajectories corresponding to different air masses were processed. Size, morphology, and chemical composition of some individual aerosol particles were determined by FEG-SEM/EDS (Field Emission Gun-Scanning Electron Microscopy with Energy Dispersive X-ray Microanalysis). Results on aerosol composition and individual element composition for samples from different air masses give the possibility of inferring transport of aerosol with different characteristic in different air masses origins in the Atlantic Ocean atmosphere. High amounts of aerosol in samples from North Africa with high concentrations of Fe, Zn, Mn, Ca, Al and K suggest the influence of dust from Sahara and Sahel region. Nonetheless, association of S with Mg in some particles could be from volcanic emissions from basaltic magmas locally existing. These last particles also appear on air masses from North America. In this last air masses high concentration of C suggest long-range transported pollution from combustion process. In Europe particles with Fe, Al, Ca, Ti, K, Na and Cl in individual particle analyses indicates a distinct mineral dust influence with marine aerosol enrichment. These air masses have some biological material as pollen. Local air masses rich in particles with Br, Na, K and Cl suggest a predominance of marine aerosol. Some particles with high concentrations of Al could be from local soil contamination. In all air masses particles smaller than 1-3 μm are predominant signifying long-range transport aerosols, as expected.

Keywords — Aerosols; North Atlantic Atmosphere; SEM-EDS; Azores

1 Introduction

The last few decades have witnessed increased interest in the occurrence, magnitude and distributions of natural and anthropogenic aerosols. This is due to their known direct and indirect effects on the earth's climate and thus their influence on the earth–ocean–atmosphere system [1], and to the role that the aerosol particles may have on human health [2].

The atmospheric aerosol contributes to about 10^{-9} – 10^{-7} of the mass of the air, which 80 % of the mass is in the troposphere and more than half of their mass is concentrated in the first 5 km layer [3]. In the North Hemisphere is estimated that about 96 % of the total aerosols emissions are from natural emissions, where marine salt and biogenic elements contributes with approximately 1443 Tg/Year and natural mineral dust with 1800 Tg/year. On North Atlantic, Atlantic Ocean and dust from North Africa are the main contributors, but volcanic emission and biogenic are also significant [4,5]. The other 4 % of emission result from anthropogenic emissions, where biomass combustion contributes with approximately 28,3 Tg/year, fossil combustion 28,4 Tg/year and other anthropogenic indirectly activities contributes with 70Tg/year [6].

In North Atlantic mineral aerosol have his main source from the dust of Sahara and also Sahel region in North Africa. Mineral aerosols from this dust could cross the Atlantic in 5-7 days. The altitude of the dust layer could arrive up to 6 km, but over the Central Atlantic Ocean is developed mainly in the first 4 km layer [7,8]. Silicate are the most abundant particle type (65-85%), however dust also carries large amounts of other elements (REE, Al, Ca, Fe, Sc and Sm) that contributes to sediments and soil composition on the deposition areas [9]. Dust from Sahara/Sahel region could also transport particles with origin different as the geological. High enrichment factors of some pollutants elements in dust from Sahara/Sahel suggest a mixing process of the pollution aerosols from Europe with the mineral aerosols [10].

Volcanic emissions also contribute with significant impact on the mineral emissions on North Atlantic. More than two-third of the world's volcanoes are in tropical regions in Northern Hemisphere, and as a consequence emissions of gases, specially volcanic sulphates, increase the

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global aerosol concentration in atmosphere. In the Azores area volcanoes from the Mid-Atlantic Ridge are mainly basaltic with magmas rich in Mg and Fe and poor in Si [11].

In all area don't exists significant human activity that increases significantly the anthropogenic aerosol concentration. Although as the West and East boundary of North Atlantic are extremely industrialized and urbanized, atmospheric long-range transport could affect aerosol increment throw some particularly events with the direct plume transport from that affected areas. The major source of anthropogenic aerosols is the combustion of fossil fuels to produce electricity. The second major source is the incomplete combustion of fuel in all forms of transportation. Other amounts of anthropogenic are attributed to the incineration process, mining and other diversity of industrial process.

Emissions of anthropogenic aerosols are in general higher in Europe than in North America partly due to a higher number of diesel-powered cars in Europe. However as the main transport pathway on North Atlantic is from West to East, atmosphere is most affected from anthropogenic aerosols from North America [12].

Under the anthropogenic emissions biomass combustion is one of the most important sources of aerosols. Globally is one of the major sources of carbonaceous material, also designated as black carbon, and is probably on of the most reliable troposphere tracers of the transport of contaminants from biomass combustion areas. Anthropogenic biomass combustion includes both the agricultural combustion the combustion for heat production and combustion on forest fires. Biomass combustion primarily contribute to the regional background particulate matter concentration, however some studies confirms the significance of such emissions on long-range transport [13].

The intercontinental aerosol transport in North Atlantic is strongly affected by horizontal weather processes of air masses in long-range distances and also vertical weather processes on the source local. These dynamic behavior are determined by: 1) Evolution of the pressure fields along Atlantic Ocean, represented by the North Atlantic Ocean index (NAOi). This index is calculated by the difference between atmospheric pressure in Azores and in Iceland; 2) the semi-permanent anti-cyclone on North Atlantic and sub-tropical area; 3) The evolution of West flow along the meridian latitude, which in fact is ruled by the NAOi; 4) air fluxes migrations from the polar boundary to the south; 5) and tropical cyclones from lower latitudes.

This study aims to study the Lower Free Troposphere (LFT) aerosol at the individual particle level. For that one of the assigments consist in the chemical characterization of the aerosols particles in the LFT. SEM-EDS and NAA were selected for the analysis of the selected sampled air masses.

Samples were collected in Pico Mountain in Pico Island placed in the Atlantic Ocean. Aerosols were collected at PICO-NARE observatory summit. The contribution of local anthropogenic sources is very low and the long-range transport observation is expected to be obtained since the site is in the pathway of air masses travelling in low troposphere (2225m) from surrounding continents (African, North Africa, North and Central America).

2 EXPERIMENTAL

In PICO-NARE station, the aerosol samples with particles with all ranges of aerodynamic diameters were collected in quartz filters (manufacturer: Pallflex®; type: Q250F) by the automated, self-contained Aethalometer (model AE31), for periods of approximately 24 h. The air-intake volume was around 7.6 m^3±0.3 m^3 to an average flow rate close to 8.47±0.44 $L.min^{-1}$. [14].

The filters from PICO-NARE station (blanks and samples) were cut from the strips in circular forms with an area of 0.950±0.086 cm^2 each. After FEG-SEM/EDS (Field Emission Gun-Scanning Electron Microscopy with Energy Dispersive X-ray Microanalysis) Nuclear Activation Analysis (NAA) was done. Each sample was irradiated for 7h with a neutron thermal flux of 3 x 10^{12} cm^{-2} s^{-1} together with one disc (125 μm thick and 5 mm diameter) of a 0.1% Au-Al alloy as comparator. After irradiation, samples and blanks decayed for 4 to 6 days and were then measured for 7 h; after this measurement samples decayed for 4 weeks more and were again measured for 7 h.

All gamma spectra measurements were done using liquid nitrogen cooled hyperpure germanium detector (1.8 keV resolution at 1.33 MeV and 30% relative efficiency), connected to 4096 multi-channel analyzers. The gold alloy discs were measured for 5 minutes, also with the same detector, 7 days after the end of the irradiations. The elemental composition of the aerosol samples was determined by k_0-standardised, instrumental neutron activation analysis – k_0-INAA [15-18] and calculations of elemental concentration with the k_0-IAEA software [19].

For this study, based on the backward trajectories, only 4 samples were selected, each one representing different air masses origins. The selected filter for Europe air masses was collected on 14th July 2005, for North America on 19th of May 2005, for North Africa on 8th April 2005 and for Tropic Cancer on 11th July 2005.

A Field Emission Gun-Scanning Electron Microscope (JEOL 7001) coupled with an Energy Dispersive X-ray Spectrometry (Oxford light elements INCA Energy 250) equipped with backscattered and secondary electron detectors and in EDS detection system (EBSD detector) at IST-UTL (Instituto Superior Técnico – Universidade

Técnica de Lisboa) was employed for acquiring the x-ray spectra in order to quantify the elemental composition of each particle from its x-ray spectrum, produced by the electron beam. Particle interaction, in a semi-quantitative analysis based on elemental standards. The filters was mounted into an aluminium FEG-SEM stub using conducting top. It was coated with a thin Au-Pd film (<10ym) to achieve higher quality secondary electron images. An accelerating voltage of 15-20kV beam and accumulation time of 20s were used. The acquisition time of 30-80s. The control software localises the particles from the image and performs an x-ray measurement within each particle. The intensities of the characterising peak in the spectra are determined by the top-hat filter method.

In the 4 samples, 27 individual particles were analysed, however they are representative of particles presented in each filter.

3 RESULTS

A study of air-masses trajectories in all sampling days of the total collection campaign was done, by displaying 10 days backward trajectory in order to establish their main directions [20]. In LFT, origin of air masses are attributed to long-range transport from North-America (49%), Arctic (12%), Local marine area (10%), Europe (9%), Central America (9%), Tropic-Cancer (7%) and Africa (3%).

One trajectory representative of the four most relevant air masses origins in terms of aerosol deposition were calculated. Figure 1.A) confirm an air mass transported from Europe no 14th July 2005; 1.B) an air mass transport from North America on 19th May 2005; 1.C) an air mass transport from Tropic Cancer area on 11th July 2005; 1.D) an air mass transport from an area close to North Africa on 8th April 2005.

These events identified with Hysplit Model carried particles with different morphologies and different chemical compositions. Figure 2a) and 2b) shows an overview of some individual particles on filters from each episode.

Higher amounts of aerosol in samples from North Africa with high concentrations of Fe, Zn, Mn, Ca, Al and K suggest the influence of mineral aerosol from Sahara and Sahel region. Nonetheless association of S with Mg in some particles could be from volcanic emissions from basaltic magma locally existing. These last particles also appear on air masses from North America.

Almost all particles of the air masses from North America appear with high concentration of C when compared with the others particles, suggesting longe-range transported pollution from combustion process in North America.

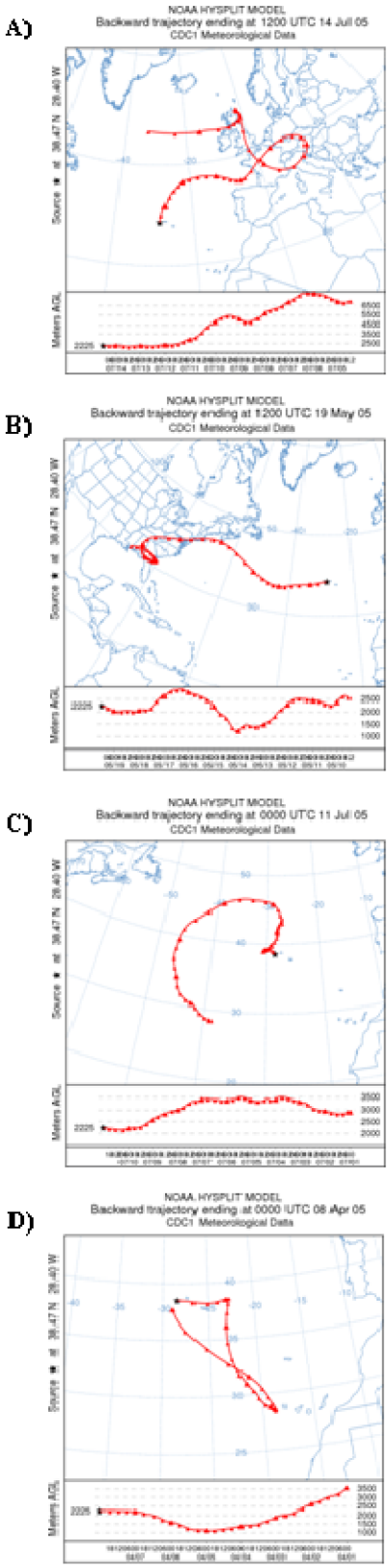
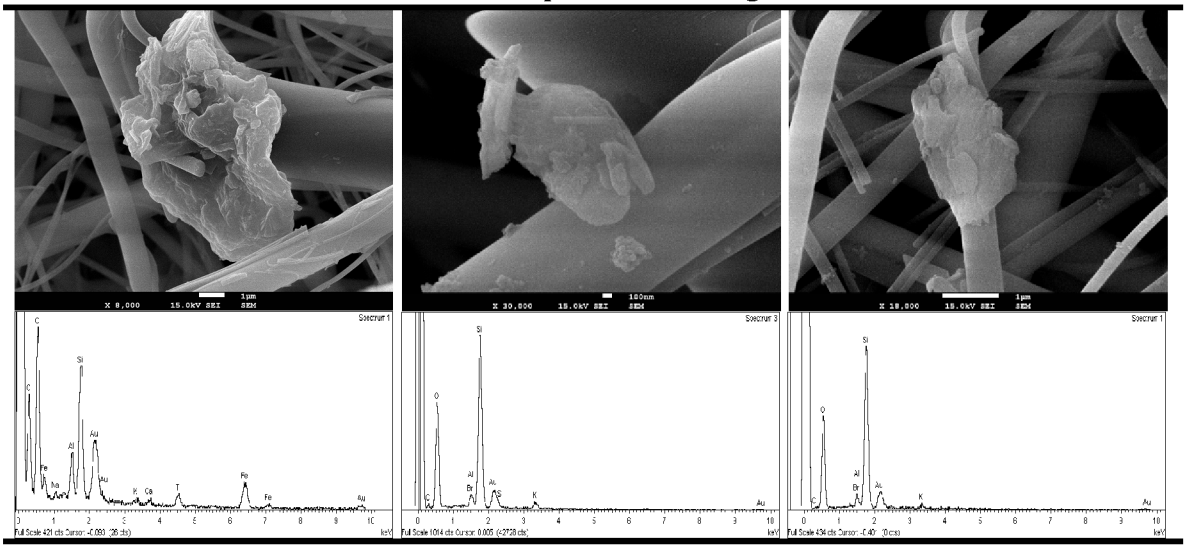
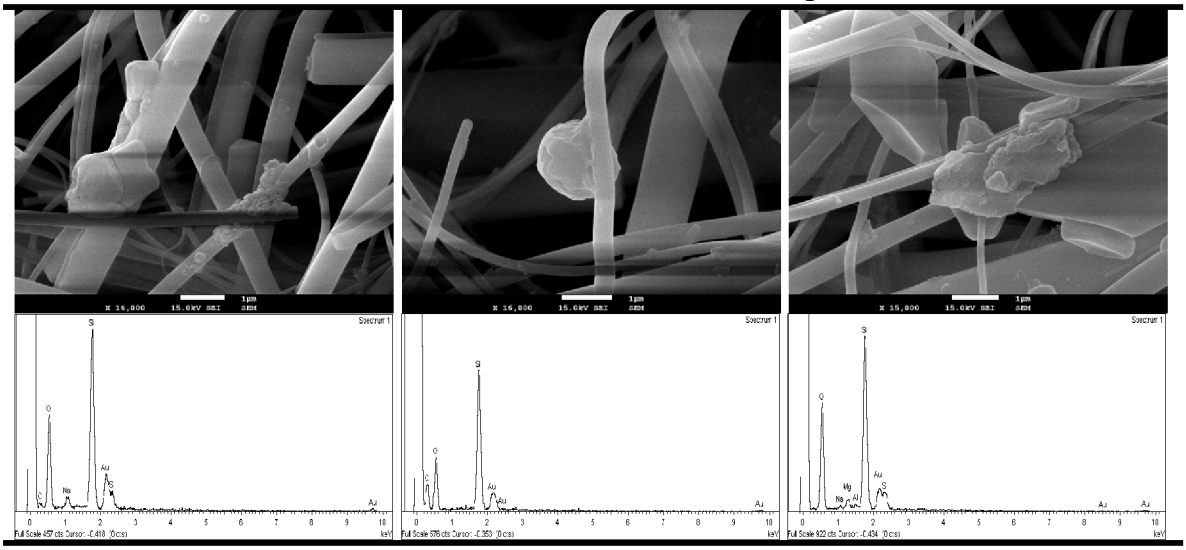


Fig. 1. Backward trajectories ending in PICO-NARE station (Midle North Atlantic), calculated with Hysplit model from NOAA. A. Europe air mass origins ending in 14th July 2005; B. North America air mass origins ending in 19th of May 2005; C. Tropic Cancer air mass origins ending in 11th of July 2005; D. North Africa air mass origins ending in 8th of April 2005.

EU – Europe air mass origin



AM – North America air mass origin



TC – Tropic Cancer air mass origin

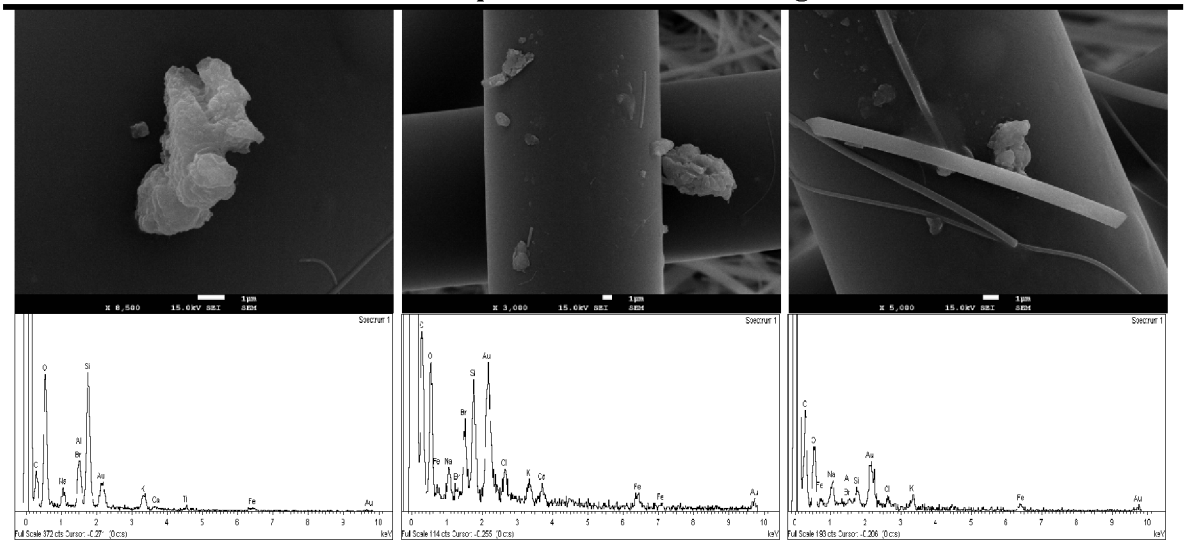


Fig. 2a. Examples of some secondary electron images (acquired with FEG-SEM) and elemental analysis of the typical airborne particles of the different air masses origins (EU – Europe; AM – North America; TC – Tropic Cancer) by energy dispersive x-ray analysis (EDS).

AF – North Africa air mass origin

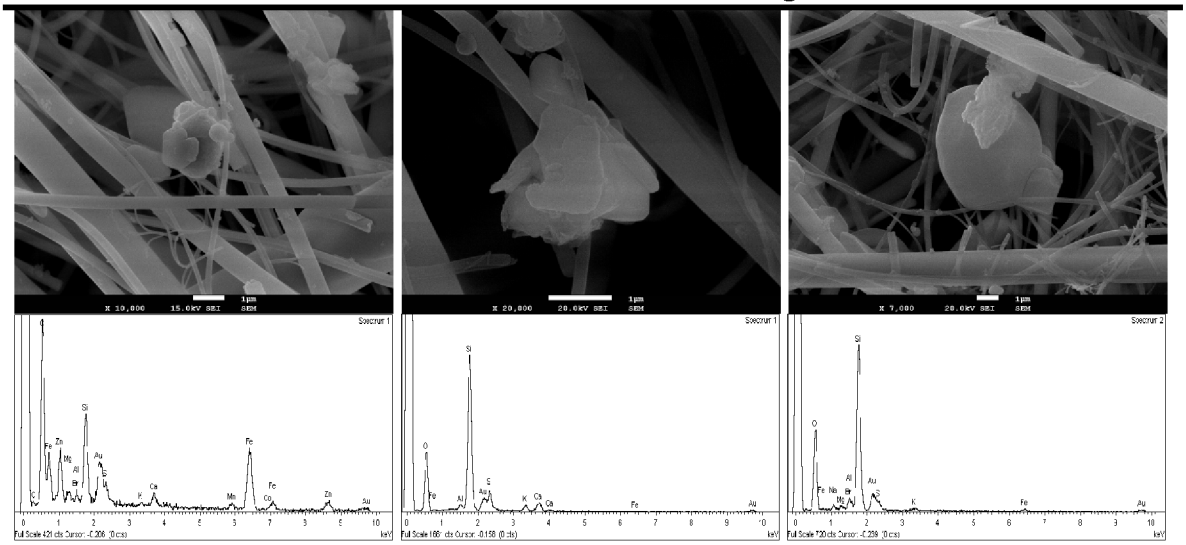


Fig. 2b. Examples of some secondary electron images (acquired with FEG-SEM) and elemental analysis of the typical airborne particles of air masses with origin in North Africa (AF) by energy dispersive x-ray analysis (EDS).

In air masses from Europe, particles with Fe, Al, Ca, Ti, K, Na, Cl and S indicates a distinct mineral dust influence with marine aerosol enrichment. Sulphur presence suggests also an anthropogenic contamination. This air mass has some biological material as pollen.

Table 1. Elemental concentrations (ng.m^3) in aerosol samples of the different air masses episodes.

	EU	AM	TC	AF
Ag		7.09±(6)	2.24±(18)	
Br				99.1±(40)
Ca	76700±(28)			
Co		0.650±(7)	0.434±(6)	
Cr	128±(4)	122±(3)	116±(3)	119±(3)
Cs		0.098±(28)	0.041±(37)	
Eu		0.036±(41)		0.032±(23
Fe	423±(20)	444±(10)	772±(19)	711±(28)
Hf			0.49±(38)	0.18±(17)
La			1.10±(27)	
Na				553±(38)
Rb			1.41±(33)	
Sb		49.3±(3)	32.8±(7)	
Sc	0.42±(30)	0.39±(45)	0.37±(17)	0.43±(26)
Se	2.49±(28)			
Tb		0.0032±(40)		
Zn	30.9±(7)	27.8±(13)	33.0±(11)	29.9±(11)

Air mass with Tropic Cancer origin is rich in particles with Br, Na, K and Cl indicates, as expected, a predominance of marine aerosol.

Mostly of the particles from all air masses are within 1-3 μm, signifying longe-range transport aerosol.

Concentrations of 17 different elements were determined by INAA as summarized in Table 1. Particularly for Fe, good agreement has been observed in chemical concentrations and abundance in some particles. The higher concentration of Fe is observed fro North Africa and Tropic Cancer air mass which is almost one order of magnitude higher than North America and Europe samples. This put on evidence the mineral contribution from Sahara and Sahel dust, which have been already confirmed in other studies. For all the other chemical elements due to the missing values no good conclusion could be achieved in order to compare different air masses. Although high levels of Se in Europe air masses and Sb in America air masses corroborates the high influence of anthropogenic emissions. This was also reported in Freitas, et al.

4 CONCLUSIONS

During the aerosol collection of the 4 selected days in FT in Middle North Atlantic Ocean, samples were analysed by automated FEG-SEM/EDS and INAA, which allowed the determination of the concentration of aerosols in filters and in some particles of the different air masses origins. For Fe a good agreement was found between the chemical composition of the sample and particles and this air mass type. The North America air masses, predominant in this area, are dominated by particles with high C abundance and high Sb concentration,

suggesting combustion processes contamination. One other hand, North Africa air masses appear with particles rich in mineral aerosol from Sahara and Sahel dust suspension and with high concentration of Fe. Air masses from Europe also present particles with elements that indicates mineral aerosol influence, however with significantly abundance of Cl, Na and S that suggest influence of marine and anthropogenic aerosol, respectively. This air mass also has rich high level of Se. As excepted particles on air masses from Tropic Cancer are rich in marine elements.

Association of S with Mg in some particles identified indicates aerosols from volcanic emissions.

Mostly of the particles from all air masses are within 1-3 μm size, This put in evidence the presence of longe-range transport aerosol in Azores from mineral, marine and anthropogenic sources.

The authors of this study focus the necessity to improve the research on the interpretation of aerosols origins in Middle North Atlantic. This will be done in further publication.

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