Lower Free Troposphere Aerosol Elemental Composition at Central North Atlantic Region

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INTRODUCTION

The Azores archipelago comprises nine islands (2335 km^2), which span over 600 km in an overall ESE-WNW direction (36º55'-39º43' N; 25º00'-31º15' W). The archipelago is thus an ideal platform for watching significant deposition episodes in the area and, especially, for tracking the regular oceanic transit of air masses from the surrounding continents – Africa, Europe and North-Central America.

Fig 1. The Azores archipelago in the context of the North Atlantic Ocean.

METHODOLOGY

The PICO-NARE observatory (38.470ºN, 28.404ºW; 2225 m AMSL), which includes the seven-wavelength aethalometer (model AE31), is an automated, self-contained, experimental station located near the summit of the Pico mountain.

The AE31 instrument has been operated with quartz-fibre filter tapes, reinforced with a non-woven polyester support layer as a strength binder (manufacturer: Pallflex®; type: Q250F).

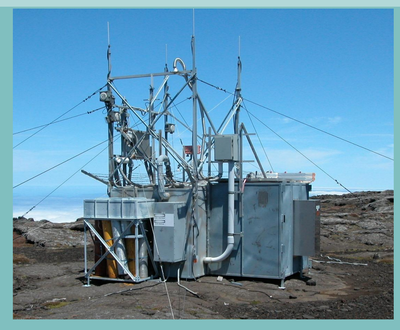
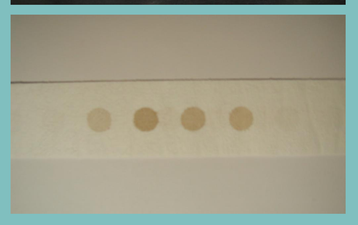


Fig 2. PICO-NARE experimental site (2225 m AMSL) near the summit of the Pico mountain (2351 m AMSL).



Aerosol samples (PM_{10}) were collected from 15 July 2001 to 18 April 2004. All elemental determinations for the present study were carried out at the Portuguese Research Reactor of the Technological and Nuclear Institute (ITN-Portugal).

Each sample or blank set was irradiated for 5-7 hours at a thermal-neutron flux of about 10^{13} n·cm^{-2}·s^{-1}. After irradiation, measurements were after 4-6d and 2-3w. All gamma spectra were acquired on a high-purity germanium detector (1.85 keV resolution at 1.33 MeV; 30 % relative efficiency).

Fig 3. Instrumental set-up for the quartz-fibre filter tape on site and an exposed section of the tape after removal at the laboratory (four identifiable spots).

RESULTS

	Br	Co	Fe	Hf	Mo	La
N	302	233	154	152	120	170
% Total	71	55	36	36	28	40
Mean	17.1	0.83	275	0.13	13.6	0.23
Median	1.34	0.49	85.8	0.090	8.94	0.094
SD	88.6	2.01	711	0.15	42.5	0.51
Minimum	0.015	0.00048	6.71	0.00093	0.023	0.0016
Maximum	1227	28.6	7978	1.35	469	4.40
	Na	Sb	Sc	Sm	U	Zn
N	186	154	136	127	256	145
% Total	44	36	32	30	60	34
Mean	477	22.8	0.054	0.14	0.78	10.4
Median	789	16.2	0.012	0.048	0.34	5.63
SD	1129	28.6	0.20	0.44	1.94	27.3
Minimum	1.40	0.0013	0.00037	0.0015	0.0022	0.059
Maximum	8341	257	2.23	3.81	20.0	276

Table 1. Number of samples for an element (*N*), proportion of samples for an element to the total analysed samples (all in ng.m^{-3}), referring to the whole collection from the PICO-NARE site, July 15, 2001, through April 18, 2004 (425 aerosol samples).

G.I	Sm	La	Fe	**G.II**	Hf	Co	**G.III**	Br	**G.IV**	Br	**G.V**	Mo
La	0.93	–	0.87	Na	–	0.51	–	–	Na	–	U	–
Sc	0.69	0.87	0.98	–	–	–	–	–	–	–	–	–
Fe	0.69	–	–	–	–	–	–	–	–	–	–	–
Co	0.96	0.86	–	–	–	–	Co	0.96	–	–	–	–
Zn	0.49	–	–	Zn	–	0.48	Zn	0.50	–	–	–	–
Br	0.97	0.85	–	–	–	–	–	–	–	–	–	–
Mo	0.99	0.86	–	Mo	–	0.97	Mo	1.00	–	–	–	–
Sb	0.52	–	–	Sb	0.68	0.56	–	–	–	–	–	–
U	0.80	–	–	U	–	0.70	U	0.81	–	–	–	–

Table 2. Significant results of the correlation-coefficient matrix ($r \geq 0.5$) for elements associated into the five identified groups at PICO-NARE (Freitas et al. 2007).

-High concentrations of Br and lower Na concentrations (one order of magnitude).

-This divergence may be due to an added anthropogenic component of Br (volatile element)

-The anthropogenic elements As and Sb (volatile elements) show higher concentrations

G.I – Related to an anthropogenic origin (Br, Sb and Zn), as well as Co, Mo and U of probable crustal sources.

G.II – Other than good correlations between Hf and Sb, and Co and Sb, includes also good correlations for Mo, Na, U and Zn.

G.III – The former high degree of association between Br and Zn in still exists, and now Br appears highly correlated with Co, Mo and U too.

G.IV & G.V – There are no significant associations within.

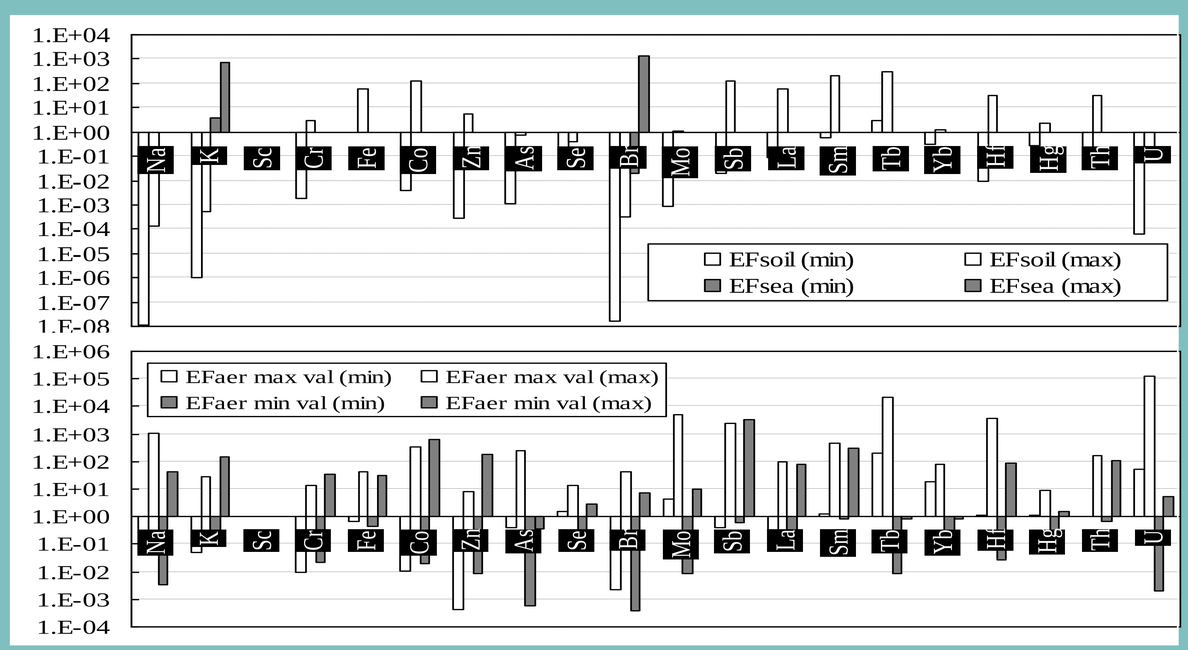
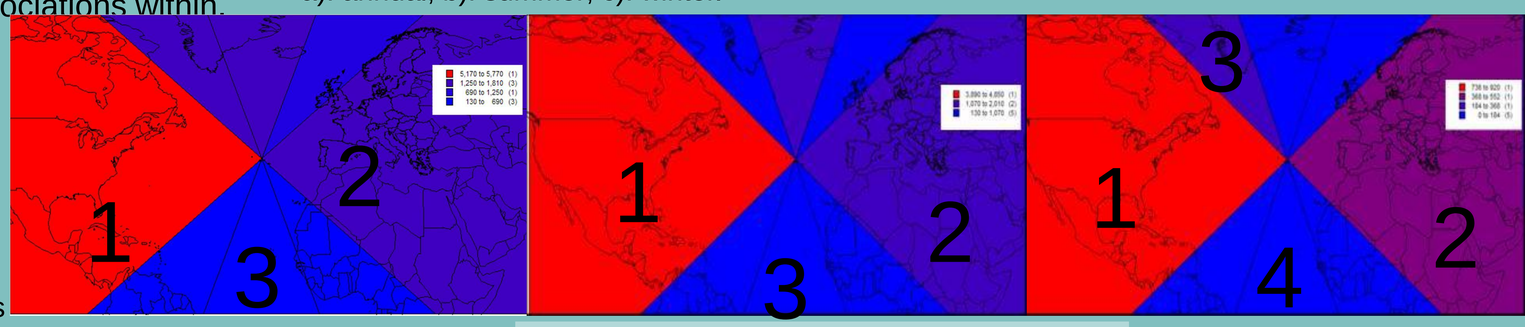


Fig. 4. Crustal and aerosol enrichment factors relative to scandium as the reference element.

Fig. 5. Directional prevalence of air masses reaching the Azores at 100 m above the PICO-NARE. a): annual; b): summer; c): winter.



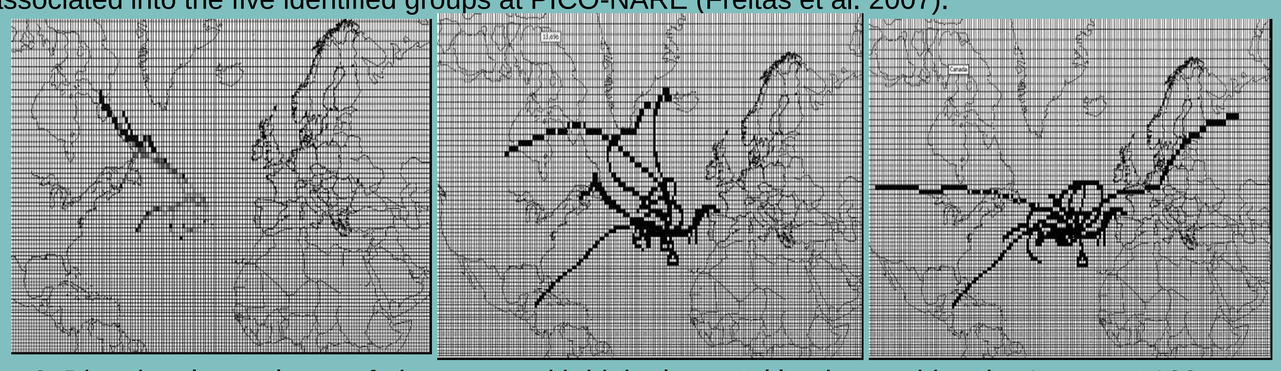


Fig. 6. Directional prevalence of air masses with high elemental loads, reaching the Azores at 100 m above the PICO-NARE observatory. a): arsenic; b): antimony; c): uranium.

CONCLUSIONS

Concentrations are in the order of magnitude of a moderately polluted urban-industrial site. Elements are predominantly entrained by air masses from North-Central America, and to a lesser extent from Europe and North Africa.

PCA and PMF assigned sources related to pollution (traffic, fossil-fuel combustion, mining, industrial processing) and to natural occurrences (crustal, Saharan episodes, marine).

Although data uncertainties are relatively high due to the small masses collected in the filters and impurities in them, PMF – which includes the uncertainty – did not prove better than PCA when missing data are replaced by arithmetic means of the determined values for each element.