Elemental composition of air masses under different altitudes in Azores, central north Atlantic

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Abstract Between 8th July 2002 and 18th June 2004, aerosol samples were collected in Azores. Their inorganic composition was obtained by neutron activation analysis in order to study the differences of aerosols in two atmospheric altitudes of the central north Atlantic: (1) PICO-NARE observatory (Lower Free Troposphere-LFT) at Pico mountain summit (38,470°N, 28,404°W, 2,225 m a.s.l.) in Pico Island, Azores, where air masses from the surrounding continents (Africa, Europe, Central and North America) pass through, carrying aerosols with anthropogenic (Sb, Br, Mo, U, Se and Tb) and/or natural emissions (Fe, Co, La, Na, Sm, Cr, Zn, Hf, K and Th); (2) TERCEIRA-NARE station (Marine Boundary Layer) at Serreta (38,69°N, 27,36°W, 50 m a.s.l.), in Terceira Island, Azores, where natural aerosols (I, Cl, Na, Br and other soil related elements) are predominant. However, a combined interpretation of the data points out to a co-existence of the anthropogenic elements Sb and Mo, eventually with similar origins as the ones passing Pico Mountain summit. Very high concentrations and enrichment factors for Sb, Mo and Br in LFT, higher than the ones found in other areas, confirm atmospheric long-range transport mainly from the west boundary of north Atlantic; this may indicate eventual accumulation and persistence of those elements in the area due to the presence of Azores high pressures or the Hadley

cells effect. A significant correlation between Fe and Yb and the enrichment of rare earth elements (La, Sm, Tb and Yb) and Th in LFT aerosols, both reflect a mineral dust intrusions from north Africa (Sahara and Sahel region).

Keywords NAA · k_0 INAA · Aerosol · Atmosphere · North Atlantic · Marine boundary layer (MBL) · Free troposphere (LFT)

Introduction

The last few decades have witnessed an 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 [1–6], and to the role that the aerosol particles may have on human health [7, 8].

The atmospheric aerosol contributes to about 10^{-9} – 10^{-7} of the air mass, with 80% of the mass in the troposphere; more than half of its mass is concentrated in the first 5 km layer [9]. In the North Atlantic it is estimated that about 96% of the total aerosol emissions are from natural emissions: marine salt, biogenic elements and natural mineral dust. Volcanic emission is also significant. The remaining 4% result from long-range transport anthropogenic emissions, including biomass combustion, fossil combustion and other anthropogenic indirect activities [10]. The marine aerosol is characteristic of north Atlantic atmosphere, but its appearance is restricted to the marine boundary layer (MBL) that ranges altitudes between 850 and 2,000 m, depending on the latitude and the annual period. In Azores area, in summer, MBL ranges between 850 and 1,100 m and in winter between 900 and 1,700 m [11–13]. The

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composition of marine aerosol usually reflects the composition of seawater at the surface layer of the oceans; it is usually associated with larger water fractions, which results in physical changes as volume modification, aerodynamic diameter and optical properties. Therefore the marine aerosol easily changes its chemical composition by reacting with components of other sources [14, 15]. Marine aerosol in north Atlantic is commonly associated to high concentration of sulphur probably originated from biogenic, anthropogenic and volcanic (observed on the Atlantic Mid-ridge) emissions [5, 16]. Mineral aerosol has the dust of Sahara and the Sahel region, both in north Africa, as its main source, contributing with approximately half of all mineral aerosols observed in the north Atlantic atmosphere [17–21]. The altitude of the dust layer could reach up to 6 km, but over the central Atlantic ocean it is developed mainly in the first 4 km [18]. Silicate is the most abundant particle type (65–85%); however dust also carries large amounts of other elements (REE, Al, Ca, Fe, Sc and Sm) [20, 21]. Dust from Sahara/Sahel region could also transport particles with origin other than the geological one. High enrichment factors of some pollutant elements (sulphur) in dust from Sahara/Sahel suggest a mixing process of the pollution aerosols from Europe with the mineral aerosols [18]. With particular weather conditions dust from arid and semi-arid regions of central Asia could also reach the north Atlantic, through the dust transported over Greenland [22]. Volcanic emissions also contribute with significant impact to the mineral emissions in north Atlantic. In the Azores area volcanoes from the mid-Atlantic ridge are mainly basaltic, with magmas rich in Mg and Fe and poor in Si [23]. The western and eastern boundaries of north Atlantic are extremely industrialized and urbanized, contributing by long-range transport to the aerosol increment. Among the anthropogenic emissions, biomass combustion is one of the most important sources of aerosols. The seasonality of concentrations of aerosols from biomass combustion on north Atlantic depends on the source area. During summer months in the Boreal forest of north America and south Europe forest fires occur, bringing carbonaceous aerosols and other particles to the north Atlantic [24, 25]. Some plums from Siberian forests have also been reported as reaching the north Atlantic [26]. In winter period, in Florida Peninsula, particular episodes of dry weather favor the increase of forest fires [27]. It is also during winter that aerosols from biomass combustion are higher in Europe mainly because of the fossil combustion for heating [26].

In general, aerosols reach the central north Atlantic in different vertical layers, depending of the air mass origins and aerosol characteristics [28]. However mechanisms of mass compensation could favor the penetration of particles in the anticyclone and their deposition over the central

north Atlantic. The maximum annual aerosol concentrations are in summer [19, 27].

This study intends to discuss elemental concentrations in air masses, which reached the central north Atlantic (Azores archipelago) in both Lower Free Troposphere (LFT) and MBL from 2002 to 2004. The climate of the archipelago is strongly influenced by the Azores anticyclone and the north Atlantic drift of the Gulf Stream, with high humidity and precipitation, which induce much milder temperatures than in other regions of the same latitude with similar oceanic temperate climate. The LFT site (2,225 m) is the PICO-NARE observatory in Pico Mountain in Pico Island which is the Portuguese highest peak placed in the Atlantic ocean. The MBL site (50 m high) is TERCEIRA-NARE station which is located in the western coast of Terceira Island, at 100 m from the coast line. TERCEIRA-NARE station is 100 km away from PICO-NARE observatory, based on their longitudes.

Experimental

In PICO-NARE station, the aerosol samples with particles of all ranges of aerodynamic diameters were continuously collected in quartz filters (manufacturer: Pallflex[®]; type: Q250F) by the automated, self-contained Aethalometer (model AE31), for periods of approximately 24 h, from 8th July 2002 to 18th June 2004. The number of analyzed filters—384 filters—corresponds to an irregular periodicity (27% in spring, 41% in summer, 20% in autumn, 12% in winter). Furthermore, the collected air volumes varied between 0.21 and 80.9 m³. The average of the collected air volume and the average of the flow rate were, respectively 4.31 ± 0.07 m³ and 3.3 L. min⁻¹ between 8th July 2002 and 17th September 2003, and 8.47 ± 0.44 m³ and 5.9 L. min⁻¹ between 18th September 2003 and 18th June 2004. Due to the remote setting of PICO-NARE and local weather conditions, instrumental maintenance was performed twice a year only [29].

At TERCEIRA-NARE station, aerosol particles below 2.5 µm in diameter (PM_{2.5}) were weekly (7-day samples) collected on pre-fired quartz fibre filters with a high volume sampler, from 8th July 2002 to 22th June 2004, the same collection period of PICO-NARE station. The total number of analyzed filters is 62 filters, corresponding to some interruptions between October 2002 and June 2004. The average of the collected air volume was 10.1 ± 3.1 m³.

The filters from PICO-NARE station (blanks and samples) were cut from the strips; each filter presented a circular form with an area of 0.950 ± 0.086 cm². Portions of the filters from TERCEIRA-NARE (blanks and samples) were cut. The samples and blanks were analysed by neutron activation analysis. For that, they were put into

Table 1 Descriptive statistics of aerosol samples from the MBL and LFT on north-Atlantic for the period 8th July 2002–18th June 2004 (ng m^{-3})

	TERCEIRA-NARE (MBL)					PICO-NARE (LFT)					Mean Ratio (MBL/LFT)		
	Mean	N	Median	Minimum	Maximum	STDEV	Mean	N	Median	Minimum		Maximum	STDEV
Na	39,923	53	22,214	85.4	215,544	48,996	599	123	77.3	0.12	8341	1316	66.6
K	2318	42	1577	14.9	10488	2241	635	9	841	22.8	959	363	3.7
Sc	0.29	60	0.15	0.0025	4.30	0.60	0.027	73	0.0095	0.00025	0.32	0.056	10.7
Cr	58.5	40	21.2	0.65	415	89.0	6.08	28	0.544	0.037	74.4	15.1	9.6
Fe	1227	70	696	1.23	23,188	2888	182	128	60.7	6.71	1909	306	6.7
Co	1.24	65	0.58	0.044	8.60	1.70	0.75	131	0.34	0.00047	5.51	1.02	1.7
Zn	88.6	70	47.2	1.06	1315	172	12.3	35	3.20	0.092	219	37.1	7.2
As	1.64	19	1.50	0.53	3.60	0.80							
Se	2.36	37	1.78	0.377	8.90	1.99	0.76	43	0.44	0.15	5.88	0.97	3.0
Br	165	67	62.2	10.3	1420	248	13.8	253	6.79	0.049	167	25.4	11.9
Rb	3.73	54	2.24	0.14	27.5	4.80							
Mo	115	52	92.9	3.92	859	125	5.63	25	2.54	0.023	24.2	5.94	20.4
Sb	0.73	66	0.62	0.017	2.80	0.60	20.9	43	9.72	0.0013	152	32.5	0.03
Cs	0.15	31	0.13	0.039	0.40	0.10							
Ba	334	28	114	7.58	2024	514							
La	2.42	23	1.50	0.04	22.0	4.50	0.16	80	0.061	0.00032	1.55	0.27	15.6
Ce	9.91	7	2.49	0.77	49.3	17.5							
Nd	6.24	6	3.20	0.82	17.1	6.60							
Sm	1.30	34	0.55	0.00090	15.5	2.70	0.24	29	0.059	0.0076	2.97	0.58	5.5
Eu	0.14	49	0.11	0.0087	1.10	0.20							
Tb	0.15	22	0.10	0.011	0.40	0.10	0.064	34	0.026	0.0070	0.66	0.12	2.3
Yb	0.42	6	0.45	0.14	0.70	0.20	0.18	36	0.037	0.0040	3.18	0.54	2.3
Hf	1.87	23	0.94	0.050	9.80	2.40	0.15	28	0.060	0.0092	0.71	0.20	12.7
Hg							0.91	14	0.060	0.037	8.51	2.34	
Ta	0.16	26	0.07	0.00040	1.70	0.30							
W	1.27	15	1.07	0.50	3.20	0.70							
Th	0.88	13	0.73	0.15	2.90	0.80	0.19	14	0.083	0.0019	0.78	0.23	4.6
U	1.12	37	0.69	0.078	6.60	1.20	0.86	160	0.39	0.031	9.86	1.48	1.3
Al	9057	35	6206	291	30963	8319							
Cl	65,552	48	16,191	233	636,029	123,001							
Mg	487	47	194	14.4	12071	1814							
Ti	769	35	349	3.56	6529	1241							
V	17.3	43	15.2	1.50	51.9	10.8							
I	22.0	19	15.9	7.34	60.3	15.2							

N number of samples with values for the element, STDEV standard deviation

aluminium foil and irradiated with discs of an 0.1% Au–Al alloy (125 μm thick; 5 mm diameter) as comparators. The irradiation time was 7 h with a neutron thermal flux of $3 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$. After irradiation, the aluminium foils were removed, the samples and blanks decayed for 4–6 days and 4 weeks and each time were measured for 7 h. The gold alloy discs were measured for 5 min, also with the same detector, 7 days after the end of the irradiations. Short irradiations with neutron thermal flux of $6 \times 10^{11} \text{ cm}^{-2} \text{ s}^{-1}$ were also done in the TERCEIRA-NARE filters. 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 4,096 multi-channel analyzers. The elemental composition of the filters was calculated with the k_0 -IAEA software [30–34]. The reference material “Air Particulate on Filter Media” (NIST-SRM[®] 2783; PM2.5 on a polycarbonate filter membrane) was analysed following the same procedure; the accuracy was within 5–15% [36].

The enrichment factor (EF) of the chemical element X in the aerosols relatively to the soil was calculated using Sc as the normalizing element and the composition of the soil collected at a depth below 0–10 cm at the same site [35], according to the expression: $\text{EF}_x = [X/\text{Sc}]_{\text{filter}}/[X/\text{Sc}]_{\text{soil}}$.

STATISTICA[®] StatSoft Inc. 8.0 was applied for exploratory, correlation and multivariate data analyses.

HYSPLIT software [37] was applied to obtain backtrajectories of air masses.

Results and discussion

Table 1 shows the elemental concentrations at PICO-NARE and TERCEIRA-NARE; concentrations of 19 and 33 chemical elements could be determined respectively. In

both layers—LFT and MLB, high amplitudes of concentrations during the sampling period were found, except for the concentrations of Al, As, Cs, I, K, Sb, Se, Tb, Th, V, W, Yb in MBL, and K in LFT, all with low variances.

Based on the 10 days backtrajectories of the sampling days, the following was observed: (1) in LFT, the origin of the 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%); (2) in MBL, the origin of the air masses is mainly from local marine area (90%), Tropic-Cancer (8%) and Europe (2%). These distinct characteristics could explain the high ratios between the element concentrations averages of the two layers. With the exception of Sb, all elements have higher mean concentrations in MBL than in LFT. Sodium concentration is almost two orders of magnitude higher in MBL than in LTR which was expected due to the closeness to the ocean and it is in accordance to reported values in other studies in oceanic areas and different altitudes. Other elements which are one order of magnitude higher in MBL than in LTR are Sc, Br, Mo, La and Hf. On other hand, Sb which has much higher concentration in LFT, may be due to the accumulation of anthropogenic aerosol undergoing long-range transport in the LFT layer Fig. 1.

The daily aerosol concentrations of PICO-NARE were weekly averaged according the week sampling periods of TERCEIRA-NARE. Correlation analysis between data of both stations show no significant correlations (not shown), suggesting that the air masses in both LFT and MBL have different element enrichments sources. However, it may also be due to the fact that in LFT and MBL all particle sizes and the particles below 2.5 μm were collected respectively. Enrichment factors were calculated to assess the elements with other origin than the crustal one and are

Fig. 1 Representation of the experimental stations in the context of north-America and Europe boundaries and of the atmosphere layers

Fig. 2 The bar in the middle of each box represents the median of the data. The range of the box is from the 25 to 75 percentile. The whiskers extend from 10 up to 90 percentile. Points above the 90 percentile are plotted individually as outliers. **a** Crustal enrichment

factors relative to Scandium in MBL (TERCEIRA-NARE) at 50 m a.s.l. **b** Crustal enrichment factors relative to Scandium in LFT (PICO-NARE) at 2,225 m a.s.l.

shown in Fig. 2. Considering that the concentration data show high variability, the graphic presentation identifies the amplitude between 25 and 75% of the EF values on the non-outlier range, the outliers and the extreme values. In this approach we focus on the mean, further publications will discuss the events related with the extreme values. The EF factors below 10 are considered to show a strong correlation to the crustal signature. The EFs between 10 and 100 indicate a moderate enrichment above crustal levels and EFs above 100 indicate that the element is significantly enriched and is originated from other natural or anthropogenic emissions.

Concerning the MBL, the elements Cl, I and Mo show high EFs and Au, Ba, Br, Cr, Na, Sb have moderate EFs. Br, Cl, I, and Na have potential marine origin. Some studies refer some photoreactions and low residence times in the atmosphere that explain these results [38]. The Sb values are moderately enriched, however in some sporadic events the extreme values reflect an enrichment of 2 or 3 order of magnitude, suggesting depositions from LFT coming from high altitude long-range transport processes. Sb may also be due to local traffic.

In LFT, with exception of Co, Fe and La, all other elements present EF above 100. Nevertheless, only Br, Mo,

Table 2 Element concentrations (ng.m³) with EF higher than 100 in MBL and LFT, and in other remote and urban areas

	This study		Remote area			Urban area	
	PICO-NARE	TERCEIRA-NARE	Himalayan Pakistan	Bering sea Artic	Mace head Ireland	New York state USA	Lisbon Portugal
Sb	20.9 ± 32.5	–	0.54	0.206		0.4	2.3
Br	13.8 ± 25.4	–		1.416		1.7	13.4
U	0.86 ± 1.48	–		0.178		0.010	
Se	0.76 ± 0.97	–	2.35			0.91	17.4
Tb	0.064 ± 0.12	–		0.007		0.058	
Th	0.19 ± 0.23	–	1.45	0.112		0.012	
Mo	5.63 ± 5.94	115 ± 125		0.090		0.20	
I	–	220 ± 15.2			36.2		2.6
Cl	–	65,000 ± 123,000	692	1585		25	930

Sb, Se, Tb, Th, U, and Yb are highly enriched. The EF values of Br and Sb reach 1,00,000, putting in evidence the large influence of anthropogenic emissions from polluted areas reaching the Azores area; the contamination levels are higher than in some highly polluted areas, reflecting some type of accumulation process. This phenomenon was previously referred by Freitas et al. [39]. Comparing the minimum and maximum EF values, Br concentrations with higher amplitude than the Sb ones could mean that they are more related with particularly emission events, while Sb values suggest background enrichment. An identical trend is observed for Se. Fossil combustion and traffic, both long transported, may be the origin [39, 40].

The magnitude of the enrichment between the two layers is different, except for Mo and Sb both with high enrichment. This fact puts in evidence the possibility of aerosol co-existence and same origins.

Table 2 shows the concentrations of the elements that are enriched in both layers and the concentrations of these elements in other remote and urban areas. Comparing to total suspended particles at remote site such Himalayan Mountains (Pakistan) [41] or Bering Sea (Arctic) [42] the concentrations at PICO-NARE are two orders of magnitude higher for Mo and Sb, one order of magnitude higher for Br and Tb and similar magnitudes for U. Se and Th concentrations are lower in PICO-NARE when compared with other remote areas. Mo and Sb have higher concentrations in this location (one order of magnitude) even when compared with urban areas of north America [43] and Europe [44].

In TERCEIRA-NARE, high concentrations of Cl and I confirm the marine suspended aerosols which influences the atmosphere at this altitude. Concentrations of Mo are even higher than in PICO-NARE, but lower EFs point out a crustal influence.

All the extreme concentration values observed in the enriched elements in LFT occur in summer season, particularly between July and August, in agreement with other

authors which identify high aerosol concentrations during summer [19, 45, 46]. On the other hand, concentration values of high enriched elements in MBL were identified in winter season, particularly during March and October, when the weather conditions favor the suspension of marine aerosols from ocean surface.

Conclusions

In the LFT, the air masses were classified as contaminated by anthropogenic elements coming from north-America and Europe, taking into account the aerosol enrichment in some trace elements and their high concentrations when compared with similar data from moderately-polluted urban and industrialized areas of North Atlantic coastal areas of Europe and America continents. Very high concentrations and EFs for Br, Mo and Sb, higher than in other globe areas, confirm atmospheric long-range transport, mainly from the western boundary of north Atlantic, not only by the direct plume transport from those extremely industrialized and urbanized areas, but indirectly via a possible accumulation and persistent emission of those elements in the area, due to the presence of Azores high pressures or the Hadley cells. Europe also contributes with similar components, with lower frequency due to the preferential wind directions from west. An additional contribution, even with less predominance, is related to mineral dust intrusions from north Africa (Sahara and Sahel region) with the enrichment of some typical elements as the rare earth elements (La, Sm, Tb and Yb) and Th.

Based on EF values, the MBL is mainly dominated by marine elements (Br, Cl, I, and Na) and local suspended soil particles. This cleaner layer of atmosphere, when compared with LFT, is influenced by two other factors with non-natural origin. One is the high enrichment and elemental concentrations of Mo. In Freitas et al. [39], it is

referred the strong association with U in a compositional profile that could fit a number of uranium processing operations in north America. Mo is also present in LFT, but in much less amount. The other common enriched element in MBL is Sb. The two common elements put in evidence the possibility of aerosol co-existence and reflection of the same air masses origins in north Atlantic atmosphere at different altitudes.

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