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Chemical Characterisation of Marine Aerosol in the Azores

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Abstract. Ground-level concentrations of particulate matter with less than 10μm in diameter were measured in Azores Archipelago, mid-North Atlantic Ocean. Three intensive research campaigns took place between April and August 99. Observed average concentrations were 3.28±2.16 μgm^{-3} for non-sea-salt sulphate, 0.98±0.72μgm^{-3} for nitrate and 0.57±0.44μgm^{-3} for ammonium. The average value for non-sea-sulphate is higher than levels previously reported for other North Atlantic sites. The higher variability in non-sea-salt sulphate data collected in Azores Region most likely reflects a contribution due to active submarine volcanoes near the collection site (10-20 miles).
We tried to make the connection between mass ratio sulphate/chloride maximums and maximum volcanic activity using seismic data. Average ratio between organic carbon and black carbon concentrations is 4.1±1.9.

1 Introduction

Understanding the physical and chemical properties of marine aerosol particles is crucial because the role these particles play in a number of atmospheric processes. Marine aerosols affect climate directly through scattering and absorption of radiation and indirectly as they can act as cloud condensation nuclei and thus influence the albedo of clouds. In addition, marine aerosol particles play an important role in the cycling of various elements through the atmosphere.

Many aspects about the origin of marine aerosols and their impact on atmospheric processes are still poorly known at present and this lack of understanding stands in part from the relatively few measurements which have been performed in the most pristine areas of the earth.

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In order to improve our knowledge about the marine aerosol characteristics and formation, an atmospheric baseline station was established on the western coast of Terceira Island-Azores (latitude: 38°41'26''N; longitude: 27°21'15'' W; altitude: 50 m, about 15 Km of Angra do Heroísmo, the main city of Terceira island, with 20000 inhabitants). A wider description about the characteristics of the station can be obtained from Rodrigues et al. (1999).

Until now, as far as it is known, no extensive data related to the ground level aerosol measurements exists in the Azores Region, with exception of the measurements during the ASTEX-MAGE studies made by Harrison et al. (1996).

A preliminary survey of average values for the major water soluble compounds and black and organic carbon of the airborne particulates during the period April 21 to August 1, 1999 is presented in this paper.

2 Experimental

Since April 1999 particulate samples have been collected at Terceira coast, using a High-Volume sampler equipped with a size selective inlet, and a quartz fibre filter (20cm x 25cm), pre-treated and washed as described on Harrison and Pio (1983) were used to sample different particle species (less than 10μm), grabbed by a constant flux of air (1.14±0.04 m^3min^{-1}).

The suspended particle mass in the atmosphere was determined by weighting the filter, before and after sampling, in a constant humidity environment. The precision of mass measurement was 0.0001g with an average reproducibility of 0.003 g.

Sampling of airborne particulate started over 48h periods, from April 21 to June 14, 1999. The low levels of black carbon found in these samples forced the sample time to be increased to 96h.

A known portion of the exposed filter was immersed in deionised bidistilled water, and water-soluble compounds extracted with an ultrasonic bath. The extracted solution was analysed for the following components: Cl^-, NO_3^- and SO_4^{2-} by high performance liquid chromatography; Na^+, K^+, Ca^{2+} and Mg^{2+} by flame atomic absorption; and NH_4^+ by UV-spectroscopy.

Black carbon (BC) and organic carbon (OC) were measured at the University of Aveiro by thermal desorption/oxidation to CO_2 and analysis by non-dispersive infrared spectrophotometry as described by Pio et al. (1991).

3 Results and Discussions

A total of 22 samples were collected. The charge balance between cations and anions in the PM10, give the correlation Eq.(1),

$$\Sigma[ANI]=(0.96\pm0.04)\Sigma[CAT]+(-0.04\pm0.02) \quad (1)$$

where $\Sigma[CAT]$ represent the sum of cations concentration and $\Sigma[ANI]$ the sum of anions concentration in microequivalent per cubic meter. The intercept value of (-0.04 ± 0.02 $\mu eq\ m^{-3}$) and slope of (0.96 ± 0.04 eq/eq) suggests that the measured ionic species constitute the larger fraction of water-soluble ions in the Azorian aerosol.

The main components in the PM10 suspended mass are presented in the Table 1.

Table 1. Average concentrations for marine aerosol ($\mu g\ m^{-3}$)

	Mean	Std dev	n	Max	Min	a)	b)
TSP	34.72	14.26	22	70.86	15.47	66.2*	
Chloride	10.20	8.97	22	30.99	2.44	11.7	
Sodium	5.85	6.29	22	21.30	0.58	7.47	
Nitrate	0.98	0.72	22	2.35	0.1	1.77	0.47
Nss-Sulphate	3.28	2.16	22	8.91	0.79	3.83*	0.85±1.06
Ammonium	0.57	0.44	22	1.41	<d.l.	0.69	0.19±0.22
OC/BC**	4.1	1.9	14	10.2	2.1	3.33*	

a) Portuguese coast Pio et al. (1996).
b) Santa Maria-Azores from Harrison et al. (1996).
* Calculated from data in Pio et al. (1996).
** Adimensional

Fig.1 shows that the representation of sodium and chloride is well described by Eq.(2), obtained by fitting the experimental data with a least-squares regression,

$$[Cl^-]=(0.93\pm0.04)[Na^+]+(0.038\pm0.007) \quad (2)$$

where $[Cl^-]$ and $[Na^+]$ represents the chloride and sodium concentrations in microequivalent by cubic meter.

The composition of sea salt usually reflects the composition of seawater that exists in the surface layer of the oceans, but reactions on sea salt particles modify its chemical composition (Seinfeld and Pandis 1998).

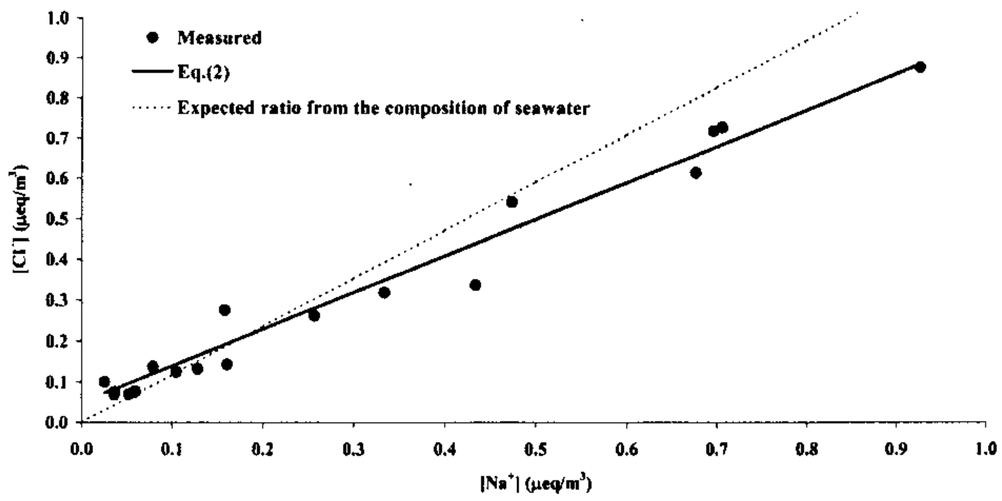

Fig. 1. Chloride and sodium dependence in the Azorian aerosol.

Fig.2 represent the mass ratio sulphate/chloride variation with time. In sea water the mass ratio of sulphate/sodium and chloride/sodium, according to Warneck (1988), are 0.252 and 1.795, respectively. Assuming these values one obtain 0,140 for the mass ratio sulphate/chloride.

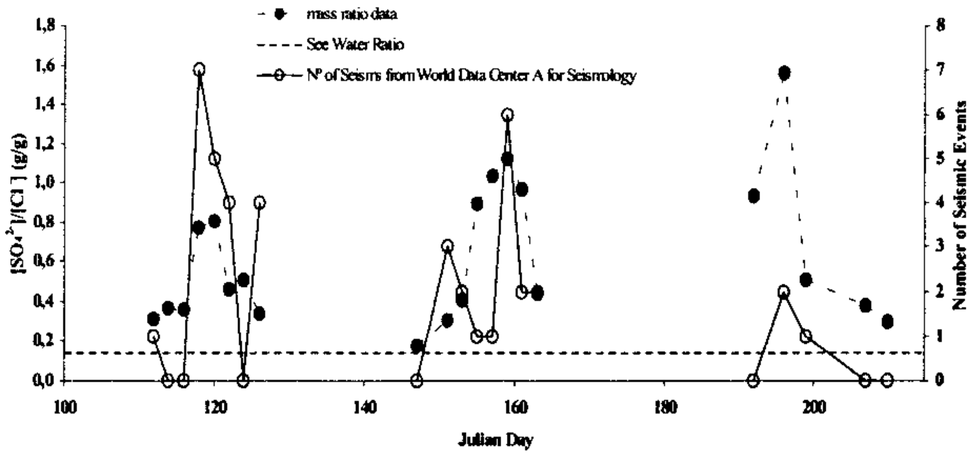

Fig. 2. Representation of the measured mass ratio of sulphate/chloride in comparison with the seismic activity on Terceira-Azores, for the same period.

Analysing Fig.(2), we believe that increases in mass ratio sulphate/chloride are associated with local emissions of volcanic sulphur. As a matter of fact, in November 1998, at about 12 to 20 km from the sample site, start to appear some submarine volcanic activity. With Fig.(2), we tried to make the connection between mass ratio sulphate/chloride measurements and the correspondent rose in seismic activity.

After the sampling period reported in this paper continuous data were taken without seismic activity in the area. We noted a decrease in the ratio sulphate to chloride. Future work is needed in the investigation of interactions between lava flows, seawater and atmosphere.

Estimation of the nss-sulphate concentration, for the periods correspondent to the minimum mass ratio sulphate/chloride (low seismic activity), are in the range 0.79 to 4.00 μgm^{-3} with a mean of 2.02 μgm^{-3}. This are in agreement with the values published by Harrison et al. (1996) for Santa Maria island, also in Azores.

4 Conclusions

Comparing the average values for the nss-sulphate and nitrate obtained in this work with others (Table 2) it seems that the value obtained is comparable with the one from Hastie et al. (1988) in Bermudas. According to Harrison et al. (1996) the high value of Hastie et al. (1988) for the nss-sulphate probably reflects the long-range transport from the North-American continent. The nss-sulfate and nitrate average values measured previously in Azores by Harrison et al. (1996) are much less than the ones obtained in this work, and we suspect that the increase in volcanic activity, namely the emissions from the submarine volcano, could explain these increase.

Table 2. Average values for nss-Sulphate and Nitrate found in the literature for the Atlantic.

Authors	Study Region	Nss-Sulphate ($\mu g\ m^{-3}$)	Nitrate ($\mu g\ m^{-3}$)
Davison and Hewitt (1992)	North Atlantic Ocean	0.24 - 1.80	
Luria et al. (1989)	Bermuda	1.0 - 1.9	
Harrison et al. (1996)	Santa Maria-Azores	0.85 ± 1.06	0.47 ± 0.39
Nguyen et al. (1974)	North Atlantic Ocean	0.5 - 1.8	
Hastie et al. (1988)	Bermuda	3.96 ± 1.63	0.88 ± 0.62
Berresheim et al. (1991)	Western North Atlantic	0.5	0.49
Pio et al. (1996)	Portuguese Marine Coast	0.44 ± 0.25	0.15 ± 0.09
This study	Terceira- Azores	3.28 ± 2.16	0.98 ± 0.72

According to Table 3, the average ratios of OC/BC for marine zones are in the range 2.1 to 10.8, with the highest value, 10.8 measured at Mace Head, a remote site. The average of 4.1 obtained in this work is in good agreement with these values, with the minimum of 2.1 and a maximum of 10.2.

Table 3. Average values for OC/BC ratios in marine zones

	Sampling site	OC/BC
Castro et al. (1999)	Portuguese Coast	2.4 – 7.3
Castro et al (1999)	Mace Head	10.8
This Work	Azores	2.1 – 10.2

The average values here published have not yet been classified according to the origin of the air masses, that work should be done in a future publication.

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