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Aerosol size-resolved trace metal composition in remote northern tropical Atlantic marine environment: case study Cape Verde Islands

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Abstract

Size-resolved trace metal concentrations of 15 elements in aerosol particles at the Cape Verde Atmospheric Observatory (CVAO) under remote background conditions were investigated through analysis of aerosol samples collected during intensive field studies from January 2007 to November 2011 using total reflection x-ray fluorescence (TXRF). The identification of the main air mass origin that influence remote marine aerosol in the northern tropical Atlantic has been investigated. In total 317 samples were collected. The dataset was analyzed according to the main air mass inflow at the station. We found that remote conditions make up about 45% of the meteorological conditions in a year at CVAO and thus the northern tropical Atlantic. Surprisingly, air masses from North America are often responsible for higher trace metal concentrations in this region.

Elements such as Zn, Pb, Cu, Cr, Ni, and V were mostly found in the submicron size fractions while elements with dominant crustal or oceanic origin such as Fe, Ti, Mn, Sr, and Rb, were found in the coarse fractions ($> 1 \mu\text{m}$). The highest metal concentrations especially for Zn (3.23 ng m^{-3}), Cu (0.81 ng m^{-3}), Sr (2.63 ng m^{-3}), and Cr (0.53 ng m^{-3}), were observed in air masses originating from North America and the concentrations were within the same concentration range to those reported previously in the literature for remote marine aerosols. Fe (12.26 ng m^{-3}), Ti (0.91 ng m^{-3}) and Mn (0.35 ng m^{-3}) showed higher concentrations when air mass came from Europe and the Canary Islands. Pb concentration was low ($< 0.20 \text{ ng m}^{-3}$) and did not vary significantly with air mass direction. The low Pb concentration is indicative of the complete phased out of leaded gasoline even in African countries. Crustal enrichment factor values decreased from fine to coarse mode particles with low values (< 4) observed for Fe, Mn, and Rb and high values (> 20) for Zn, Cu, Ni, Cr, Pb, and Se. The observed enrichment of the elements was attributed to crustal, marine, anthropogenic and biogenic sources, as well as long range transport and re-suspension. Zn, Cu and Pb were indicators of anthropogenic activities while Ti, and Sr, were indicators of crustal and marine origin,

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respectively. Oceanic emissions contributed to most of the Selenium observed. This work provides the first long term size resolved trace metals study for remote tropical northern Atlantic marine aerosols and the dataset could serve as good initiation of yearly flux estimates.

1 Introduction

Atmospheric input of trace metals is essential for marine productivity, for example, Fe, Mn, Cu, Cd, and Zn (Morel et al., 2003). The atmosphere has been recognized as a major source of metals to the open oceans (Duce et al., 1991) since inputs from river and land erosion are mostly local whereas atmospheric inputs are not localized but spread over larger area. Islands are very useful in studying deposition patterns to the open oceans since they experience similar conditions like the oceans and provide long lasting infrastructures for carrying out long and short term experiments. In the tropical northern Atlantic, the Cape Verde islands are well situated for carrying out such experiments and atmospheric conditions in this region are representative of a larger part of the northern tropical Atlantic. This was one of the principal reasons for the creation of the Cape Verde Atmospheric Observatory (CVAO). CVAO thus provides a platform for studying both remote marine aerosols as well as continental and Saharan dust dominated aerosols. Aerosol compositions being observed at CVAO are affected by mixing of air masses and the influence of aerosols from sources situated in North America, Europe or Africa. Thus the aerosol composition varies temporally and spatially in concert with meteorological conditions.

Remote conditions at the CVAO are attributed to air masses that do not come from neighboring continental Africa since such air parcels are known to carry significant amount of mineral aerosols especially during Saharan dust outbreaks. The outbreaks have seasonal patterns with peaks between December and March (Chiapello et al., 1997, 1999, 2005). The other months are dominated by remote conditions with very low aerosol loadings which could be as low as $7 \mu\text{g m}^{-3}$. During such conditions aerosol

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trace metals originate from oceanic emissions as well as long range transport from southern Europe and North America.

Previous ship cruises and other works in this region have mostly been focused on the influence of Saharan dust outflow from the African continent (Johansen et al., 1999; Buck et al., 2010a, b; Hand et al., 2004) but not much has been done to better characterize the aerosol trace metal in remote conditions which despite their low concentrations are also of importance to the marine biota.

Aerosol trace metal studies in some remote regions of the Atlantic oceans at Bermuda (Huang et al., 1996; Duce et al., 1976; Spokes et al., 2001; Witt et al., 2006) or during ship cruises (Spokes et al., 2001; Witt et al., 2006) and even in Antarctica (Weller et al., 2008) have shown that trace metals are enriched above the oceanic and crustal sources and are found in different size fractions. Anthropogenic activities that lead to emission of trace metals are usually related to high temperature processes such as smelting, fuel combustion, or waste incineration (Pacyna et al., 2007; Galloway et al., 1982). In such processes metals are mostly emitted in gaseous forms and they rapidly condense on the surfaces of particles having a high surface area leading to their likely presence in the fine mode ($< 1 \mu\text{m}$) aerosol particles (Galloway et al., 1982). Recently, there have been reports on trace metals found in marine microgels and colloids (Bertine and VernonClark, 1996; Guo et al., 2000). These gels and colloids usually less than $1 \mu\text{m}$ in size have been found to act as cloud condensation nuclei (Orellana et al., 2011). Thus, although they are not yet well characterized in marine aerosols they may contribute to the trace metal budget in the sub-micrometer aerosol particle fraction. Metals from coarse particles ($> 1 \mu\text{m}$) are mostly attributed to mechanical processes such as rock weathering, soil erosion, volcanic eruptions, or bubble bursting. Coarse mode particles are deposited faster and have atmospheric life times of up to 4 days while fine mode particles live longer and may attain life times of more than 6 days under dry conditions. In regions with low rain probability and thus less influence of wet deposition such as the Cape Verde islands and its local environment (Lee et al., 2010) such particles can readily reach the above atmospheric lifetimes (Lawler et al., 2009;

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Johansen et al., 1999). Therefore, emissions from anthropogenic activities may have significant influence on trace metal budget in this region.

Within the present study results of data collected during a series of nine intensive field campaigns from January 2007 to November 2011 on size-resolved trace metal composition in remote marine aerosols observed at the CVAO are presented. The aim of this work was to characterize the variability of bioactive trace metals such as Mn, Fe, Cu, Zn, Se, V, Cr, Pb, and Ni, evaluate their natural background concentrations, size distribution and their source origins with the help of crustal enrichment factors and back trajectory analysis in this region of the Atlantic. Major sea salt elements such as K, Ca, S, Cl were not the focus of this work.

2 Experimental

2.1 Site and sampling

Aerosol sampling was performed at the CVAO which is located north east of the island of Sao Vicente, Cape Verde and is situated 70 m from its coastline at 16°51'49 N, 24°52'02 W experiencing mostly north-easterly winds. The annual average temperature at Sao Vicente is about 25 °C and it is an arid region with a maximum of 50 mm of rainfall per year. Sample collection was done on top of a tower with an inlet height of 32 m above ground to reduce strong influence of sea spray on the collected particles. Due to the location of the station, influences from the island like orographic influences in dust sedimentation and anthropogenic emissions are negligible. Thus the collected samples are representative of a clean atmosphere over the ocean and not contaminated by materials from the islands. A picture of the CVAO station is shown in Fig. 1 with clear view of its coastline location, the 30 m high measurement tower, measurement containers and subsidiary electrical power infrastructure.

Particles were sampled using a high volume (HV) Digital (DHA 80) collector on quartz filters in 72 h periods throughout the year for aerosol mass concentration and further

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chemical analysis. During intensive campaigns lasting 4–6 weeks, size resolved sampling was carried out using a 5-stage Berner low pressure impactor with a PM₁₀ isokinetic inlet (Hauke, Gmunden, Austria) operated at a flow rate of 75 L min⁻¹ in a 24 h period with about 45 min reserved for the replacement of the samples. The impactor samples were collected on annealed aluminum foils and polycarbonate (nuclepore) foils (Wicom, Heppenheim, Germany). The nuclepore foils were placed on the aluminum foils on each impactor stage and were used for the determination of metals. The impactor stage cutoff's were as follows: stage 1 (St.₁): 0.05–0.14 μm, stage 2: 0.14–0.52 μm, stage 3: 0.52–1.2 μm, stage 4: 1.2–3.5 μm, stage 5 (St.₅): 3.5–10 μm.

After sampling, filters were stored in aluminum boxes at 5 °C at the station for 24–48 h and subsequently frozen at –20 °C. The samples were thereafter transported under frozen conditions from Cape Verde to Leipzig (Germany). To estimate the mass of the particles, the filters were equilibrated for 3 days at 20 ± 1 °C and 50 ± 5 % relative humidity before and after sampling and thereafter weighed. The mass of the filters were determined using a micro-balance (HV-filter: MettlerAT261 Delta Range, impactor foils: Mettler Toledo UMT2).

2.2 Metal analysis

Trace metal analysis on nuclepore foils was carried out using Total Reflection X-Ray Fluorescence (TXRF) S2 PICOFOX (Bruker AXS, Berlin, Germany) equipped with a Mo-X-ray source on polished quartz substrates. The nuclepore foils were cut with respect to the number of visible spots on the foils (6 spots for stage 1, 3 for stage 2, 2 for stages 3 and 1 for stages 4 and 5). Cut spots were placed on substrates and 5 μL 65 % concentrated HNO₃ and subsequently gallium (as internal standard) was added on the spots. Depending on the size fraction, different gallium concentrations were applied (10 ng for the three sub-micrometer fractions and 100 ng for the coarse mode fractions). The solution was left to evaporate at about 100 °C and thereafter the substrates containing the spots were measured. As reported by (Müller et al., 2010), the cut spot diameters are typically 6 mm and were close to the TXRF beam diameter of

10 mm. However, due to sample orientation on the substrate, samples were measured at two different angles having a difference of 90° between them in order to ensure a complete excitation of the spots. Each substrate was measured 3 times at each angle and the maximum value from the measurements at the different angles was taken as the elements value on the substrate.

PICOFOX is able to analyze elements from Al to Bi. However, in this work the focus has been only on the aerosol trace metals which are not naturally expected to reside in remote aerosols in high concentrations compared to major sea salt elements such as Cl, Br, K, S or Ca. The studied trace metals were Mn, Fe, Cu, Zn, Se, V, Cr, Pb, Ni, Ti, Rb, Sr, Ba, La, and Ce. The other trace elements not considered in this work were not detected such as elements from Pr to Tl or had concentrations below the background level for elements such as Y, Zr, Nb, Ru, Rh, Cd, Pd, Ag, Sn, Sb, Te. Due to the low crustal content in the remote marine aerosols analyzed and the high background values of Si and Al coming from the quartz substrate and aluminum foils used during the sampling, respectively, the concentrations of Si and Al could not be effectively quantified. Furthermore, the sample preparation method (e.g., the substrate heating at 100 °C) made quantification of volatile species such as Cl and Br difficult.

The blank values of the polycarbonate filters and the quartz substrates were measured (Table 1). The filter field blanks were higher than those of the substrate. The typical blank values of the quartz substrates ($n = 75$) of these elements were < 10 pg except for Fe where values were < 20 pg. A total of 20 field blank filters were analyzed during the stipulated sampling period and were prepared using the same procedure as those of the probed filters as stated above. The field blanks were filters that we deployed to the field but were not probed during the campaign. Their elemental average values were used as filter blank values (Table 1). The highest blank values were observed for Fe, Zn, and Sr and the lowest for Se, La, and Rb. Blank correction was done by subtracting blank filter values from those of the probed filters.

In principle, the detection limit of TXRF is in the picogram range but also depends on the substrate background and sample type with lower limits for very thin films compared

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to powder samples, provided the substrate surface is well polished. The method detection limit was estimated as three times the standard deviation (Std.) of the filter blank values (Table 1). For all the analyzed elements, more than 90 % of the samples had values that were above the method detection limit. However, the blank subtraction method led to uncertainties and estimation errors especially for the first impactation stage of about $\pm 25\text{--}35\%$ due to their low mass while uncertainties of about $\pm 7\text{--}15\%$ was obtained for the other stages with the higher percentage in the lower stages especially for elements with higher method detection limits.

2.3 Back trajectory analysis

Air mass back trajectory footprints for all collected samples were performed to assist in the data interpretation. 96-h back trajectories were calculated for every hour within the sample collection interval using the PC version of the NOAA HYSPLIT (Hybrid Single Particle Lagrangian Integrated Trajectory) model. The model was run in the ensemble mode with a starting height of 500 m above ground level. In the ensemble mode, offsets are applied to the meteorological field for each member of the trajectory ensemble. One meteorological grid point in the horizontal dimension and 0.01 sigma units (approx. 250 m) in the vertical dimension were used in this work. The resulting trajectory ensemble consists of 27 trajectories for all possible offsets in the x-, y-, and z-dimension. The air mass history of a 24 h sample is then described by an ensemble of 648 trajectories which provides a better description of the variability in the air mass footprint as compared to the single trajectory mode. Via a GIS approach, the meteorological and geographical data are combined in a database to produce graphical outputs for the air mass footprint. The output then provides information of the estimated air mass residence time over given geographical landscapes, e.g., over natural vegetation, marine, arid, urban, and agricultural areas. These landscapes are usually represented in the graphical output with the colors, green, blue, yellow, black and brown, respectively. Further details on the ensemble procedure and the GIS based approach can be found in (van Pinxteren et al., 2010).

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3 Results and discussion

3.1 Aerosol mass concentration

Figure 2 shows the time series of the aerosol mass concentration measured at CVAO within the time period of January 2007 and November 2011. The time interval during which intensive field campaigns and trace metal analysis were performed are highlighted in red with open triangles. Nine intensive field campaigns were performed during this period. Four of the campaigns were carried out in the winter months between December and February lasting averagely 6 weeks (i.e. KV II, IV, VI and VII) while the rest five were performed in the months of May, June, July and November lasting mostly 3 to 4 weeks. Thus a higher amount of samples were collected during the winter months as otherwise. In total, 317 samples were collected during the intensive campaigns. The temporal variability of the mass concentrations shown in Fig. 2 is indicative of the seasonal trends observed in this region with respect to the aerosol particle loading. As indicated in the figure, during the period between 23 October 2009 and 09 July 2010 sampling was done at a height of 4 m on the top of a container due to tower maintenance. Thus during this period, the aerosol mass was strongly influenced by sea spray. With the exception of the above mentioned time period, the high spikes with mass concentrations above $100 \mu\text{g m}^{-3}$ are mostly indicative of days with Saharan dust outbreak which are often observed in the winter months. The low mass concentrations below $30 \mu\text{g m}^{-3}$ are typical of remote conditions at CVAO and as can be seen from the time series, this scenario is representative of about 45 % of the year.

The variation in the mass concentrations during remote background conditions were found to be correlated with the local wind speed. Average local wind speed at CVAO lies at about $7.3 \pm 2.2 \text{ m s}^{-1}$ but might increase to $> 13 \text{ m s}^{-1}$ during stormy periods leading to variations of up to 30 % in the aerosol mass concentrations. Similar seasonal trends in aerosol loading with higher mass concentrations during the winter months in comparison to the summer months were observed in other previous studies in this region (Chiapello et al., 1995; Schepanski et al., 2009). This seasonality is attributed to

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the changing location and structure of the subtropical “Azores” high pressure system which resides to the north of Cape Verde. According to Kalnay et al. (1996), the high pressure region in winter is broader and covers a larger region from the Caribbean to the middle east thus facilitating air mass inflow from the African continent while in the summer months, the region is narrower and restricted to the central Atlantic ocean favoring north-east air mass flow from along Europe and the African coast. Despite this high pressure zones, the air mass inflow also changes within the winter periods such that air masses from Europe and North America are also observed at CVAO. Thus, the remote scenario considered in this work is not restricted to particular seasons but mainly on the daily and weekly variation of the changing air mass direction observed at CVAO.

3.2 Air mass analysis

All 317 collected size-resolved samples were characterized and analyzed for their air mass footprints. 100 of these samples were of remote conditions, that is, strong air mass influence from the Atlantic, Canary Islands, Europe and North America. The rest of the samples (217) were related to air mass outflow from or linked to the African continent especially through the Saharan Sahel corridor. The larger number of samples in this regime is justified by the timing during which most campaigns were done. Table 2 shows the classification of the samples with respect to their air mass back trajectories.

The trajectory categories were, Atlantic marine (AM), marine over the Canary Islands (MC), Marine over Europe (ME), Marine over North America (MNA), Marine with continental Africa (MCA), Saharan dust only (SS), Saharan dust and Urban areas (SU), and lastly Europe and African air mass (EA). The numbers at the bottom of the table represent the total number of times that a given category was observed including mixed situations, e.g., marine air mass over Europe and the Canary islands. In this study, only the results of the 100 samples pertaining to the remote background conditions at CVAO (AM to MNA) will be discussed. Figure 3 shows exemplary back trajectories of

four days that were representative of the air mass categories AM to MNA. Figure 3a to d represent AM, MC, ME and MNA conditions, respectively.

The Atlantic air masses mostly arrived from the North West direction and were most of the time associated with low wind speeds ($< 6 \text{ m s}^{-1}$). The back trajectory analyses reveal that these air masses usually spent little time over urban or arid regions in the last 96 h prior to their arrival at CVAO. On the contrary, the marine air masses over the Canary Islands crossed some arid and urban regions prior to their arrival at CVAO. The marine air mass from Europe had slightly higher wind speeds than both the AM and MC air masses and as shown below were mostly of North East origin. These air masses are also expected to carry fresh anthropogenic emitted particles with them. Lastly, the North America marine air masses also came from the North West with higher wind speeds than any of the other air masses, and also carried significant amounts of anthropogenically emitted particles with them. These four regimes are discussed because they are the main air mass regimes that account for the remote marine aerosol constitution at CVAO. The regimes as mentioned above have only weak seasonal trends with more remote conditions observed in the spring and summer months but no strong seasonal trend as those for mineral dust outbreaks.

3.3 Trace metal concentration

The average concentrations (standard deviations in brackets) of the investigated metals for the given air mass categories are shown in Table 3. In obtaining the average concentrations, 34 samples for the MA, 27 for the MC, 15 for the ME and 10 for the MNA air mass categories were used while the samples pertaining to the mixed scenarios were not considered. Results show higher variability of the metal concentrations (as shown by the standard deviation values) for MNA air masses in comparison to the others.

This difference may be attributed to the high wind speed ($> 13 \text{ m s}^{-1}$) that is associated with this air mass resulting to a greater mixing of different sorts of aerosols. Higher concentrations of Zn, Cu, Sr, Ba, Rb, and Cr were observed for MNA air masses

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in comparison to the others. The higher wind speed could explain the higher concentrations of Sr, Ba, and Rb since these elements are also emitted from the oceans and to a very small extend Zn, Cu, and Cr, from particle re-suspension from the surface waters (Weisel et al., 1984). However, the higher concentrations of Cu, Cr and Zn are mainly from anthropogenic activities since Zn is a strong surrogate for anthropogenic emissions (Wang et al., 2005), e.g., from combustion processes, which are common in North America.

The concentrations of other crustal elements such as Fe, Ti, and Mn, were lower for the MNA but higher for ME and MC air masses. The higher concentrations from these air masses may be due to the shorter distance the air-parcel traveled prior to arriving at CVAO, thereby, enabling an easy transportation of crustal particles over this distance. A similar tendency to that of the crustal metals was observed for Se, Ni, and V, with higher mass concentrations observed for air-parcels originating from Europe and the Canary islands in comparison to those from the other directions. For the other investigated metals including; Pb, Ce, La, Sc, no significant difference was found between their concentrations with respect to the air mass back trajectories implying their values may represent typical background concentrations in this region.

The mean concentrations of Pb in this work were low ($< 0.2 \text{ ng m}^{-3}$ and ranged from $0.01\text{--}0.46 \text{ ng m}^{-3}$) in comparison to reported concentrations of other studies but were, however, within the concentration range reported elsewhere for remote conditions. Kriews and Schrems (1998) reported median concentrations of 0.32 ng m^{-3} ($0.11\text{--}57 \text{ ng m}^{-3}$) for Pb in aerosol samples collected over the Atlantic ocean during the Polarstern cruise from Bremerhaven to Punta Arenas (Chile). Huang et al. (1996) reported arithmetic mean concentrations of 0.86 ng m^{-3} ($0.04\text{--}3.2 \text{ ng m}^{-3}$) at Bermuda while 10 yr earlier Wolff et al. (1986) had reported mean concentration of 3.6 ng m^{-3} ($< 0.1\text{--}8.7 \text{ ng m}^{-3}$) at Bermuda. Witt et al. (2006) reported Pb concentrations of, 0.19 ng m^{-3} ($0.08\text{--}27 \text{ ng m}^{-3}$), for remote northern Atlantic and 0.6 ng m^{-3} ($0.15\text{--}1.8 \text{ ng m}^{-3}$) for remote southern Atlantic during their JCR cruise. The values in this study are in good agreement with those of Witt et al. (2006) for remote northern Atlantic conditions but

deviate from those in other remote regions. Comparing the Pb concentrations from air masses from North America in this work 0.14 ng m^{-3} (0.05 to 0.23 ng m^{-3}), to those reported at Bermuda by Haung et al. (1996), it is eminent that there have been a significant decrease by about a factor of 3 in the Pb emissions from North America over this time period. This decrease is likely related to the phased-out of leaded gasoline and the improvement in technological processes that are related to Pb emissions.

In all air mass directions, iron had the highest mean mass concentration ($< 12.26 \text{ ng m}^{-3}$) followed by Zn ($< 3.26 \text{ ng m}^{-3}$), Sr ($< 2.63 \text{ ng m}^{-3}$), Ti ($< 0.91 \text{ ng m}^{-3}$), Ni ($< 0.89 \text{ ng m}^{-3}$), Cu ($< 0.81 \text{ ng m}^{-3}$), and Cr ($< 0.53 \text{ ng m}^{-3}$). The lowest concentration was observed for Co ($< 10 \text{ pg m}^{-3}$), La ($< 30 \text{ pg m}^{-3}$), and Se ($< 100 \text{ pg m}^{-3}$). The concentrations of the other elements were between these extremes. The obtained concentration range of these elements is within the same order of magnitude as those reported for other remote regions in the Atlantic and other open oceans. Witt et al. (2006) reported mean concentrations and ranges for Cu, 0.7 ng m^{-3} (0.34 – 1.42 ng m^{-3}), Ni, 0.18 ng m^{-3} (0.06 – 0.26 ng m^{-3}), and Zn, 2.56 ng m^{-3} (0.68 – 4.48 ng m^{-3}) for remote southern Atlantic conditions. For the remote northern Atlantic, concentrations for Cu, 0.58 ng m^{-3} (0.47 – 0.7 ng m^{-3}), Ni, 0.22 ng m^{-3} (0.01 – 0.42 ng m^{-3}), Zn, 2.05 ng m^{-3} (1.95 – 2.15 ng m^{-3}), and Ba, 0.42 ng m^{-3} (0.4 – 0.44 ng m^{-3}) were reported. The concentrations in this study were in good agreement with those reported by Witt et al. (2006) for remote northern Atlantic conditions. Despite the few data set used by Witt et al. (2006) in comparison to those used in this study, the concentration ranges in the two studies are within the same order of magnitude. Duce et al. (1983) reported mean concentrations for remote conditions at Enewetak of 0.04 ng m^{-3} for Cu, 0.17 ng m^{-3} for Zn, 0.08 ng m^{-3} for V, 0.12 ng m^{-3} for Pb, and 0.16 ng m^{-3} for Zn. Their mean values were generally lower than those obtained in this work but, however, fall within the concentration range observed in this study. Similarly, Spokes et al. (2001) reported slightly higher concentrations than those of Duce et al. (1983) for remote marine conditions at Mace Head but their values are still within the concentration range obtained in this work. They found mean concentrations of 1.45 ng m^{-3} for Pb, 3.87 ng m^{-3} for Zn, and

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0.66 ng m⁻³ for Mn. Weller et al. (2008) reported concentrations of 19.0 (±18.0) pg m⁻³ for Se, 1.6 (±1.3) pg m⁻³ for Ce and 0.86 (±0.7) pg m⁻³ for La for remote regions at Neumayer, Antarctica. Their concentrations were lower than those in this work which is expected due to lower anthropogenic influence in the Antarctica as at CVAO. The values for Fe, Ti and Mn were within the range of values observed by (Buck et al., 2010b) during their CLIVAR ship cruise along the Northern tropical Atlantic.

Generally, metals from crustal origin were dominant in air masses from Europe and Canary islands while elements known to be emitted from anthropogenic process such as Cu, Zn, Cr, Ni, were of long range transport with a higher concentration observed from air masses originating from North America.

In summary, we found reasonable agreement on the data of Pb, Cu, Zn, Se, Ba with those reported in the literature, however, we observe slightly higher concentrations for Ni, Cr, Sr, and lower values for Fe, Mn, Ti, V. Higher Cr, Zn, and Cu concentrations were observed only in MNA air masses while Fe, Mn, Ti, Ni, V were higher in ME and MC air masses. These results were comparable to other remote marine regions in the Pacific or southern Atlantic Ocean but are the first long term results for trace metal concentrations in remote northern tropical Atlantic marine aerosols. The small concentration variations between this work and other reported works, however, can be explained in terms of the different dominant air mass origins that strongly influence the remote environment. Although there have been other studies of trace metal concentration in other remote marine environments as cited above, we are not aware of any long term studies in the northern Atlantic of size resolved data that would allow assessment of compositional variability and aerosol solubility studies as in the present work.

3.4 Size resolved analysis

The size-resolved analysis of the investigated metals for the given air mass footprints is shown in Fig. 4. Fe, Ti, Sr, Rb, Mn, were mostly found on stages 4 and 5 (1.2–10 μm) implying that most of the mass of these metals originated from a common source of

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coarse aerosol. This tendency was for all of the air mass directions. About 85 % of Sr, 40–60 % of Mn, 70–75 % of Fe, Rb, and Ti was present in the coarse mode with a small increase in their mass fraction by about 10 % during MNA air mass influence. This increase may also be attributed to the high wind speeds usually accompanying this air mass. Despite the prevalence in the larger particles, their presence in the sub-micron particles is indicative of the presence of particles from combustion and or industrial sources in addition to re-suspension and frictional process from road traffic. Fine mode manganese may originate from high temperature combustion processes of manganese rich fuels. Ba, La, Ce, were found on all stages with a higher fraction on stages two and three for La, and on stages four and three for Ba and Ce. This implies that these elements were of mixed origin, such as from crustal, oceanic and anthropogenic sources.

Vanadium, Cr, Ni, Cu, Zn, and Pb were mostly found in the fine mode, in particular, on impactor stages 2 and 3 (0.14 μm –0.52 μm). However, more than 20 % of their mass was also found in coarse mode particles. Their broad existence is indicative of their multiple source origin including a combination of long range transport due to the long atmospheric residence time of the sub-micron particles, vehicular, and industrial emissions. With the phased out of leaded gasoline, lead concentrations may likely be of non-automotive sources related to metal industries (Allen et al., 2001; Guieu et al., 2002).

For a few elements, Cr, Ni, Cu and Zn, less than 20 % of their mass was found on stage 1 (50–140 nm). The presence of such bioactive trace metals in the submicron particle range suggest that these metals may be coming from organometallic compounds in the ocean as well as from marine colloids (Orellana et al., 2011; Guo et al., 2000) that are known to contain substantial amount of trace metals. Organic compounds containing these metals could be released from the ocean's surface micro-layer through blasting of the ocean surface during stormy conditions thereby releasing them to the atmosphere. Such organic compounds can also be long range transported from the continents. High organic matter concentrations on stage1 were observed in previous studies at CVAO (Müller et al. 2010). Selenium showed a significant coarse

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mode fraction. This occurrence may be due to the presence of biogenic material or the deposition of gaseous forms of Se on coarse particle surfaces. The demarcation between the elements present in the fine and coarse mode particles in all air mass categories is better illustrated in Fig. 5 in terms of the $PM_{1.2}/PM_{10}$ ratio. $PM_{1.2}$ is obtained as the sum of the first three impactor stages while PM_{10} is the sum of all impactor stages. The $PM_{1.2}/PM_{10}$ ratios show a uniform profile for the various air mass origins.

The deviations from the pattern are only observed for Mn, Ba, La, and Ce. Most of the metals were present in the fine mode exhibiting high $PM_{1.2}/PM_{10}$ ratios especially for V, Cr, Ni, Cu, Zn, and Pb. For Mn, the different tendencies were observed for the different air mass origin implying a significant amount of fine mode Mn particles were emitted from air masses originating from Europe and also those crossing the Canary islands. The variation in the fine to coarse mode ratio for Ba, and Ce in the different air mass origins imply that these elements had many origins or possessed significant spatial variability. In most cases, the dominantly fine mode metals were concentrated on the second and third impactor stages ($0.14\text{--}1.2\ \mu\text{m}$) and can be attributed to long range transport. Metals of crustal or oceanic origins such as Ti, Mn, Fe, and Sr show very low $PM_{1.2}/PM_{10}$ ratio being indicative of their coarse mode presence.

3.5 Enrichment factor analysis

Crustal enrichment factor (EF) analysis was applied to estimate the contributions of crustal dust to the obtained elemental concentrations in our samples. For this analysis, Ti was used as marker for mineral dust instead of iron since iron has a wider origin in oceanic regions than titanium. Wedepohl (1995) compilation of continental crust composition was used to calculate enrichment factors and crustal contribution on elemental concentrations.

For an element (Z) in a sample, the EF relative to Ti is given as:

$$EF = \frac{(Z/Ti)_{\text{Sample}}}{(Z/Ti)_{\text{Crust}}} \quad (1)$$

An enrichment factor above 2 is considered as moderate enrichment of the element and below 0.70 signifies strong depletion in comparison to the composition of the reference source. Enrichment factors between 0.70 and 2 are considered to be similar and within the error range to the reference source, implying that the elements with such factors might have originated from such a source. Figure 6 shows the enrichment factors with respect to Ti for each size fraction and PM₁₀ for the measured elements in the four main air mass directions representative of the remote conditions.

The elemental enrichment factors show similar trends in all four air mass directions with a reduction in the EF's with increasing particle size. The coarse particles were thus related to crustal emissions in comparison to the fine mode particles. From the elemental enrichment factors, three main groups of element could be observed.

- i. Group one elements include Fe, Mn, Co, and Rb. These elements had enrichment factors between 0.8 and 2 on most of the stages in all air mass directions. Their PM₁₀ enrichment factors also lied in this range indicating that these elements are associated with particles which became airborne by soil dispersion or other crustal sources. Mn showed higher EF's on stages 2 and 3 for the Atlantic marine air masses indicating that other sources than mineral dust could contribute to its presence such as from iron and steel industries (Hacisalihoglu et al., 1991). The release of manganese during smelting and use of methylcyclopentadienyl manganese tricarbonyl as an octane enhancer in unleaded car fuels may partially account for enhanced levels of fine mode aerosol manganese seen in polluted air (Wallace and Slonecker, 1997; Pfeifer et al., 1999). This could be associated to long range transport from Europe or North America since particles in this size range (140 nm to 520 nm, stages 2 and 3) can live longer than 8 days in the atmosphere.
- ii. Group two elements include Ba, Ce, La, Sr, V. These elements had enrichment factors between 2 and 20 indicating they were of mixed sources, including crustal, marine or anthropogenic sources. The lower enrichment factors were observed

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mostly in the case of marine air masses (Fig. 6a, b) indicating the elements were likely of crustal origin while the higher EF were mostly observed in air masses that crossed Europe or North America (Fig. 6c, d) before arriving at CVAO indicating that these elements were also of anthropogenic origin. The high enrichment factor for V was mostly observed on the second and third stages. The main source of atmospheric non crustal V is residual oil burning (Zoller et al., 1973) and particles from oil burning processes do have long atmospheric life times due to their small particles sizes. The high Sr enrichment factors can be attributed to its marine (Weller et al., 2008) sources.

- iii. Group three elements include Pb, Cr, Ni, Cu, Zn and Se. These elements had very high enrichment factors in all air mass directions. The high values are an indication of strong anthropogenic influence. Atmospheric Pb originates mostly from smelters or from the burning of unleaded fuel. In general, combustion processes are the major contributors for Pb which is consistent with its dominant presence in the very fine mode. Despite the phased out of leaded fuel, residual levels of Pb in air originating from Pb in gasoline are expected to persist in continental particles for decades (Brewer and Belzer, 2001). Pb can also originate from re-suspension of crustal material (Wang et al., 2005) thus explaining the lower EF with decreasing particle size observed for Pb. Ni and Cr are also emitted via combustion processes. As observed above their higher enrichment in the fine mode is indicative of emissions from combustion processes (Steinsberger et al., 1994). Their occurrence in the coarse mode may be related to natural emissions including windblown soil, vegetation or to a very small extend sea salt. Road traffic has also been found to contribute to Ni emissions with mean emission factors of about 0.07 mg kg^{-1} in Europe, suggesting that road traffic pollution might not be negligible. Similarly, the very high EF for Cu and Zn signifies their anthropogenic origin. Cu and Zn are elements that are typical of emissions from anthropogenic activities like fly ash, waste incineration and traffic (Pacyna, 1984; Pacyna and Pacyna, 2001). Their enrichment in the coarse mode indicates that the coarse



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mode particles may be originating from lower temperature industrial processes or from erosion of Zn rich soils. Cu and Zn may also have oceanic sources especially when associated with marine colloids that may be released from the marine microlayer or also from re-suspension (Weisel et al., 1984).

5 Selenium had the highest enrichment factor in all air mass directions and on all impaction stages suggesting that its presence in this region is not related to crustal fractionation or erosion. Coal fired power plants and copper smelters apparently are important anthropogenic sources for Se (Germani et al., 1981; Andren et al., 1975) and may contribute to the observed concentrations in this region especially for air masses that crossed Europe or North America before arriving at CVAO. Other natural sources like sea spray (Mosher and Duce, 1987) or volcanoes have also been suggested (Cunningham and Zoller, 1981). The sea spray could certainly account for a given fraction of the observed concentrations since Se was observed in all air mass directions. However, volcanic sources may be rather negligible since very few active volcanoes are positioned along the air mass directions observed in the work. In Cape Verde, the active volcano of Fogo lies south east of CVAO thus its influence on the remote Se concentrations observed at CVAO may be neglected. It has been postulated that heterogeneous reactions are important determinants of Se concentrations in aerosol particles. According to Mosher and Duce (1983), approximately 10 to 25 % of the Se in nonurban regions resides in the vapor phase and a significant amount of the gas phase Se evolve from the ocean with a subsequently occurrence of a gas to particle conversion in the atmosphere. Although the mechanisms responsible for this evolution were not specified, they inferred that the processes responsible for the flux of Se from the ocean to the atmosphere are biologically mediated. Amouroux et al. (2001) showed that the production of gaseous Selenium species coincide with phytoplankton blooms responsible for dimethyl sulfide (DMS) emission. They observed that the sulfur atom in DMS can be substituted by Selenium implying a close correlation between DMS and Se. Lately, Weller et al. (2008) observed a significant correlation between Se and the end products of photochemical DMS oxidation, methane sulfonate and non-

sea salt sulfate, suggesting that atmospheric Se should be closely coupled to the DMS production. Conclusively, the enriched Se in the particles can therefore be attributed to oceanic sources for the coarse and fine fraction as well as long range transported aerosol for the particles in the fine fraction.

4 Conclusions

Size resolved trace metal concentrations of 15 elements in aerosol particles at CVAO under remote background conditions were investigated in this study. The identification of the main air mass origins that influence the remote marine aerosol in the northern tropical Atlantic has been achieved. For this analysis, a total of 100 samples collected over a four year time period from 2007 to 2011 were used. Our observation revealed that remote conditions were representative of 45 % of the year's aerosol conditions at CVAO while Saharan dust and air mass originating from continental Africa accounted for the remaining 55 % of the year. The results show very low trace metal concentrations as compared to continental trace metal concentrations but, however, fall in the same order of magnitude as those observed in other remote oceanic regions. Higher metal concentrations were observed for air masses that had crossed North America or Europe before arriving at CVAO in comparison to Atlantic marine air mass. In general, the air mass from North America was also associated with high wind speeds ($> 13 \text{ m s}^{-1}$) leading not only to higher metal concentrations but also to higher aerosol particle concentration. The size resolved data of the metals show distinct distribution of the elements indicating that the particles resulted from disparate processes. In particular, elements from natural sources were primarily associated with coarse particles although other natural sources like oceanic emissions might have also been responsible for some fine mode particles. Elements from anthropogenic sources were found in the fine mode particles. Enrichment factor analysis was performed to evaluate the natural opposed to anthropogenic sources of the metals. High enrichment factors were observed for Zn, Cu, Ni, Cr, Pb and Se indicating their dominant anthropogenic over

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natural processes. In the case of Se, biogenic sources might have also been important. Elements such as Mn, Fe, Ba, Rb, had low enrichment factors indicating their predominant natural source such as soil erosion or sea spray. Our observation over a five year period at CVAO shows that the long range transport from North America as well as Europe play a key role in the supply of essential bioactive metals such as Zn, Co, Cu, Fe, Cd into the northern tropical Atlantic ocean which are constantly required for the metabolism of marine microorganisms. With emissions from anthropogenic activities dominating the trace metal budget in remote aerosols and thus the life of marine organisms in this region, it is important that caution and consideration are taken when making environmental policies on anthropogenic activities in Europe, Africa and North America. These results are expected to be representative of the trace metal content deposited to the ocean over this region and may provide useful hints on assessing the impact of these metals on processes at the ocean surface or water columns via model studies.

This work provides the first long term size resolved trace metal studies with a larger dataset for remote marine aerosol in the northern tropical Atlantic. These results could serve as a starting point for initializing model runs and estimating yearly flows of these metals in this region of the Atlantic Ocean since these results are representative of events that occurred over the last five years with some seasonal trends. Obtaining yearly flows of total and bioavailable aerosol trace metal content in this region would be useful in assessing the global input of atmospheric nutrients into the northern tropical Atlantic

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Table 1. Average blank values of quartz substrate ($n = 75$) and filter blank ($n = 20$) and overall method detection limit (MDL). All values are given in ng. Typical sampled volume was 105 m^{-3} . n.d. implies not detected.

Element	Substrate		Filter blank		MDL
	Mean	Std.	Mean	Std.	$3 \times \text{Std.}$
Ti	0.008	0.004	0.043	0.011	0.033
V	0.003	0.002	0.011	0.003	0.009
Cr	0.005	0.002	0.032	0.028	0.084
Mn	0.004	0.002	0.005	0.008	0.024
Fe	0.018	0.028	0.45	0.148	0.444
Ni	0.004	0.003	0.01	0.012	0.036
Cu	0.004	0.005	0.089	0.016	0.048
Zn	0.008	0.003	0.166	0.041	0.123
Se	n.d		n.d		
Rb	0.002	0.001	0.004	0.004	0.012
Sr	0.005	0.003	0.102	0.031	0.093
Ba	0.003	0.001	0.007	0.004	0.012
La	0.003	0.004	0.004	0.003	0.009
Ce	0.005	0.003	0.007	0.005	0.015
Pb	0.006	0.002	0.02	0.019	0.057

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Table 2. Air mass back trajectory classification of all 317 samples with the various categories representing the likely air mass origin in the last 96 h prior to arrival at CVAO. Table also shows mixed scenario, in which air mass had crossed both categories before arriving at CVAO.

Categories	AM	MC	ME	MNA	MCA	SS	SU	EA
Atlantic marine (AM)	34	6	2	2	3			
Marine over Canary (MC)		27		2		50	22	
Marine over Europe (ME)			15	2		8	25	
Marine over North America (MNA)				10		11		
Marine with continental Africa (MCA)					5			
Sahara (SS)						37	1	3
Sahara and urban (SU)							28	
Europe/Africa (EA)								24
Total	34	33	17	16	8	106	76	27

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Table 3. Average (standard deviation), minimum, and maximum PM₁₀ trace metal concentration at CVAO under remote conditions for the various air mass origins. Samples with mixed scenarios were not considered in obtaining the average values. Values are given in ng m⁻³. Range shows the lowest and highest concentrations measured in all the samples irrespective of their air mass origin. Reported column represent mean concentrations and their reported ranges in brackets.

	AM	MC	ME	MNA	Range	Reported
Ti	0.53 (0.72)	0.85 (0.6)	0.91 (0.99)	0.62 (0.27)	0.05–3.17	(0.81–6.02) ^d
V	0.14 (0.19)	0.31 (0.2)	0.31 (0.27)	0.13 (0.14)	0.01–0.82	(0.45–1.27) ^d
Cr	0.37 (0.24)	0.49 (0.22)	0.31 (0.22)	0.53 (0.27)	0.01–0.99	0.09 (0.03–0.39) ^c
Mn	0.12 (0.18)	0.35 (0.19)	0.21 (0.15)	0.09 (0.07)	0.00–0.81	(0.01–1.27) ^d
Fe	6.39 (7.1)	11.38 (6.41)	12.26 (10.4)	9.88 (7.32)	0.1–25.89	(1.4–24.45) ^d
Ni	0.32 (0.32)	0.89 (0.36)	0.64 (0.43)	0.47 (0.29)	0.01–1.5	0.18 (0.06–0.26) ^a
Cu	0.43 (0.38)	0.57 (0.26)	0.47 (0.31)	0.81 (0.41)	0.03–1.17	0.7 (0.34–1.42) ^a
Zn	1.23 (1.19)	1.01 (0.51)	0.89 (0.46)	3.23 (1.61)	0.05–4.77	2.56 (0.68–4.48) ^a
Se	0.06 (0.04)	0.1 (0.05)	0.08 (0.05)	0.04 (0.02)	0.01–0.2	0.019 (0.018) ^b
Rb	0.01 (0.01)	0.02 (0.02)	0.01 (0.02)	0.03 (0.02)	0.00–0.05	0.12 (0.04–0.46) ^c
Sr	1.14 (1.56)	2.09 (0.24)	0.66 (0.49)	2.63 (1.83)	0.01–9.25	0.29 (0.27) ^b
Ba	0.15 (0.27)	0.14 (0.1)	0.16 (0.16)	0.47 (0.35)	0.01–0.93	0.15 (0.05–0.25) ^a
La	0.01 (0.01)	0.03 (0.03)	0.02 (0.01)	0.01 (0.01)	0.00–0.1	0.00086 (0.0007) ^b
Ce	0.03 (0.02)	0.03 (0.04)	0.02 (0.03)	0.03 (0.03)	0.00–0.14	0.0016 (0.0013) ^b
Pb	0.09 (0.09)	0.15 (0.11)	0.2 (0.19)	0.14 (0.07)	0.01–0.46	0.6 (0.15–1.8) ^a

^a Witt et al. (2006) ^b Weller et al. (2008) ^c Duce et al. (1983) ^d Buck et al. (2008).

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Fig. 1. CVAO station situated at the coastline of the Sao Vicente Island in the northern tropical Atlantic with clear view of the 30 m high measurement tower, some measurement containers and a wind turbine for subsidizing electrical energy.

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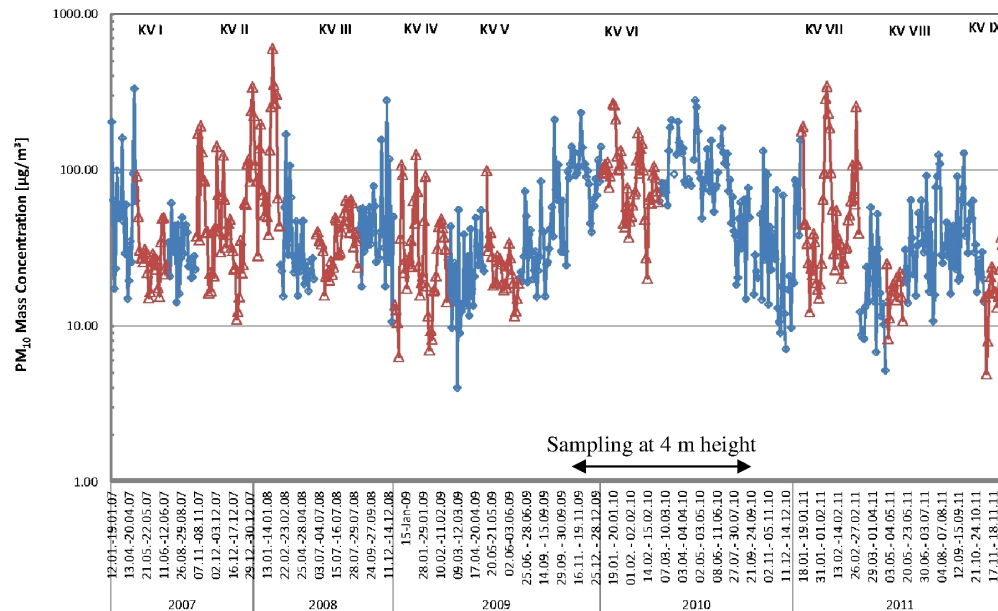


Fig. 2. Time series of PM_{10} mass concentration at CVAO from January 2007 to November 2011. Red lines with open triangles represent periods of intensive field measurements (9 in total labeled KV I to KV IX).

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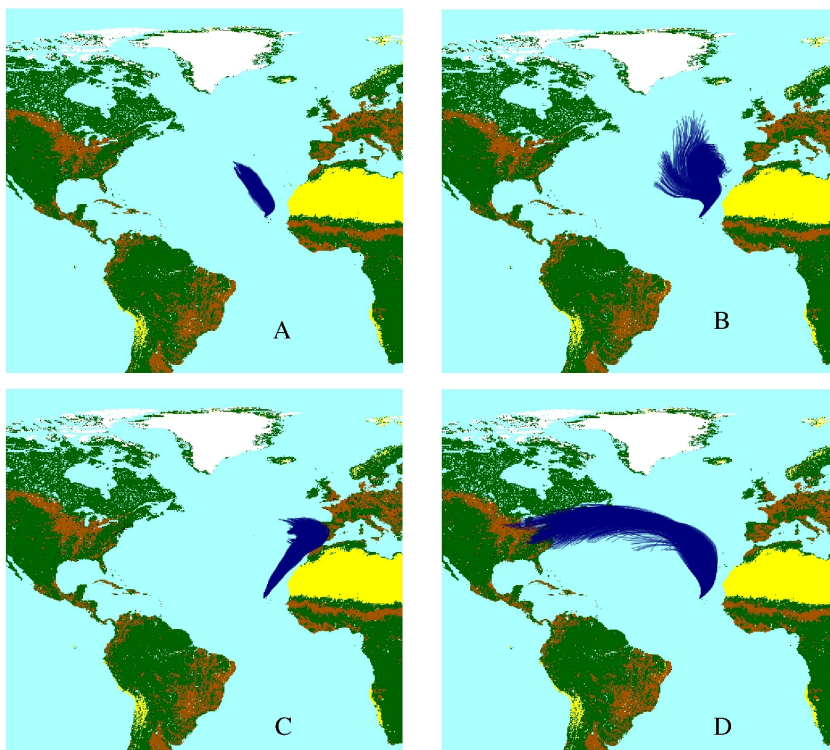


Fig. 3. Examples of 96 h air mass back trajectory ensembles arriving at CVAO. The blue, yellow, green and brown colors represent ocean, arid, vegetation and continental landscapes, respectively. **(A)** 2 May 2011: Atlantic marine, **(B)** 24 May 2009: Marine over Canary Islands. **(C)** 4 June 2007: Marine from Europe, **(D)** 2 February 2009: marine air mass from North America.

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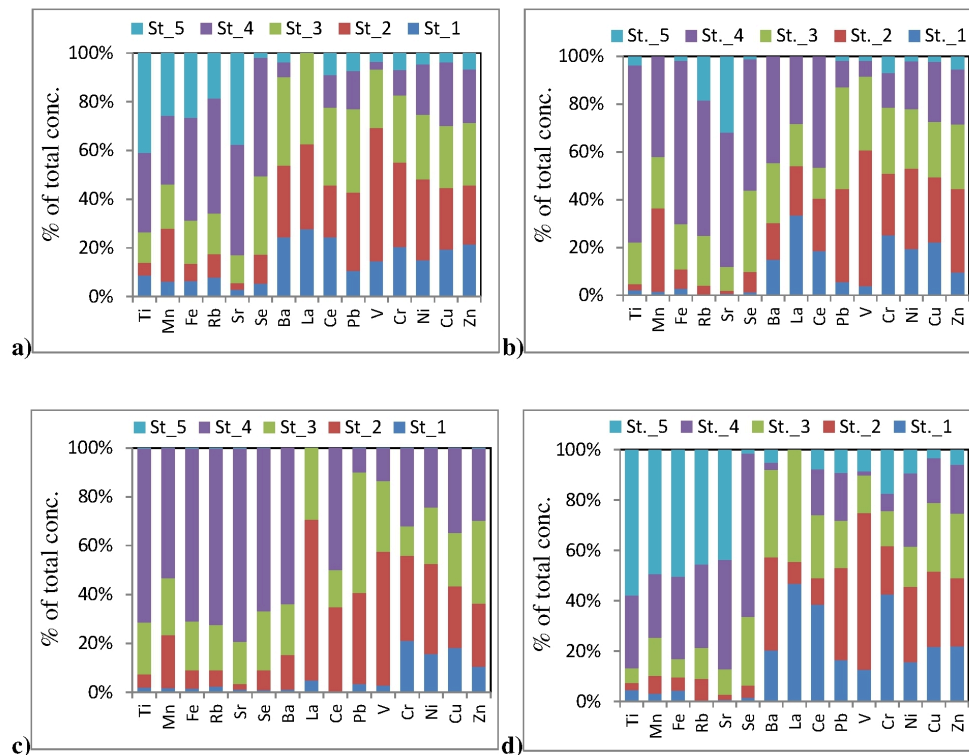


Fig. 4. Distribution of investigated elements according to their size fractions for all four air mass directions; **(a)** AM, **(b)** MC, **(c)** ME, and **(d)** MNA.

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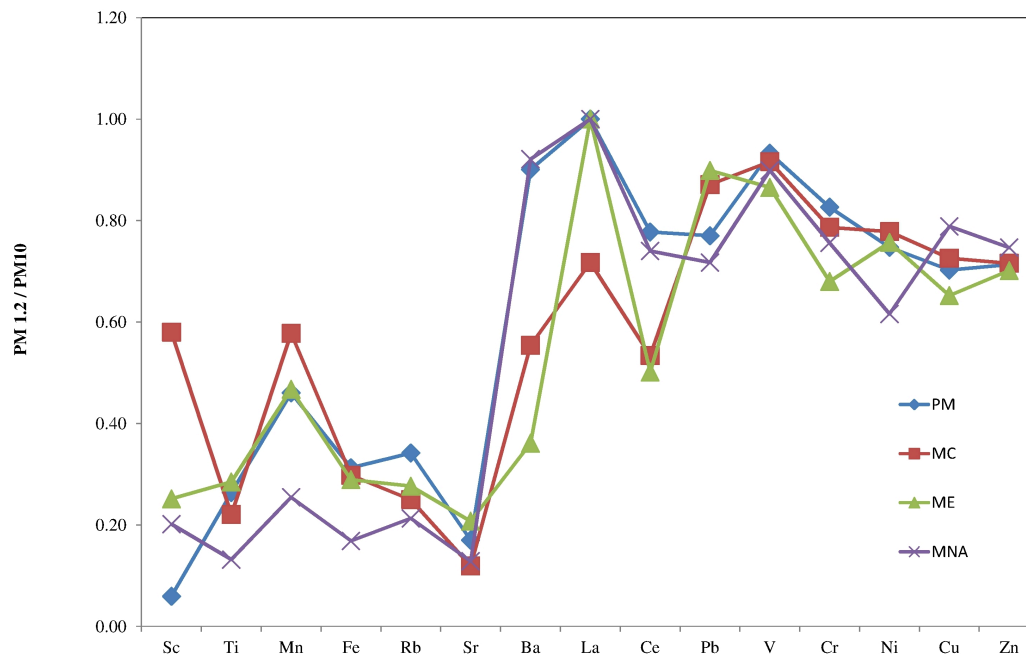


Fig. 5. Fine ($PM_{1.2}$) to coarse (PM_{10}) ratios for measured trace elements in the four major air mass footprints representative of the aerosol background at CVAO.

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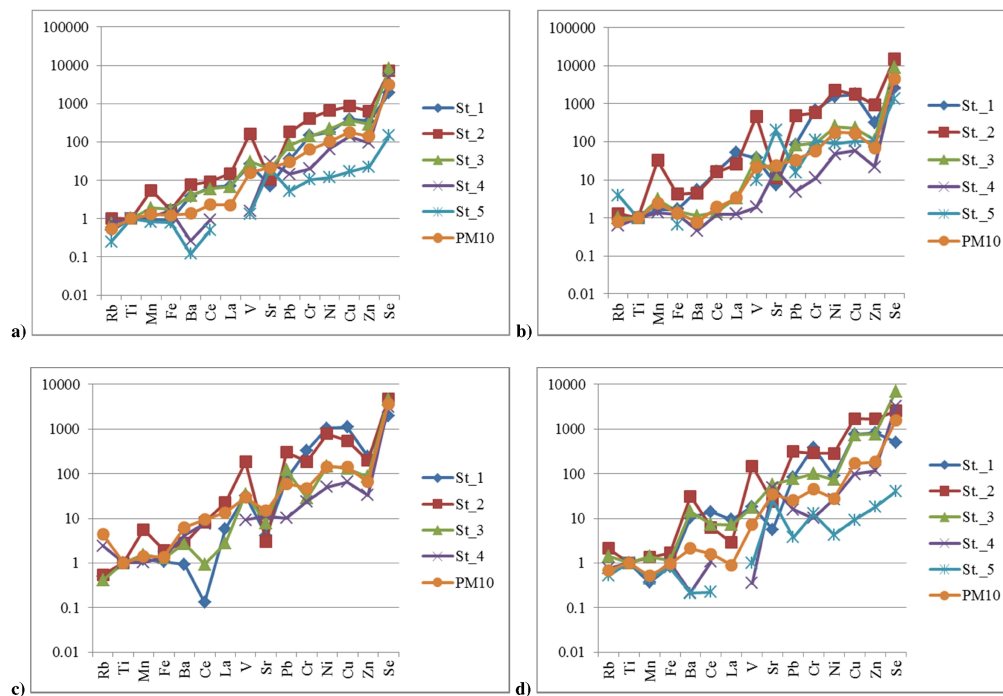


Fig. 6. Enrichment factors of the measured elements in each impactor stage and each air mass origin from **(a)** AM, **(b)** MC, **(c)** ME, to **(d)** MNA.

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