

Characterization of the aeolian aerosol from Cape Verde by k_0 -INAA and PIXE

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Abstract Due to its location on West Coast of Africa, Cape Verde is highly influenced by Sahara Desert dust events being an optimum place to observe and study the African aeolian aerosol. During 2011, particulate matter with an aerodynamic diameter lower than $10\ \mu\text{m}$ (PM_{10}) was sampled in Santiago Island and its chemical composition was evaluated by k_0 -instrumental neutron activation analysis (k_0 -INAA) and particle induced X-ray emission (PIXE). This study showed the existence of a seasonal intrusion of dust from Africa (that occurred from October to March) characterized by significant increases of PM_{10} , mineral elements and anthropogenic particles concentrations. In 2011, the PM_{10} health-based air quality guidelines defined by WHO, EU and USEPA were exceeded. Cape Verde PM_{10} composition was characterized essentially by high concentrations of elements originating from the soil (Ca, Ce, Co, Fe, K, Mg, Mn, Rb, S, Sc, Si, Sm, and Ti) and sea (Br, Cl, and Na); and low concentrations of anthropogenic elements (As, Cr, Cu, Ni, Pb, Sb, V, and Zn). k_0 -INAA and PIXE were fundamental tools for the

determination of airborne chemical elements in Cape Verde. Their multi-elemental capabilities in association with low detection limits made it possible to determine the majority of the element concentrations of environmental interest.

Keywords k_0 -INAA · PIXE · Aeolian aerosol · Sahara desert · Cape Verde

Introduction

The globally most severe events of dust re-suspension occur in Sahara Desert [1], which are responsible for the introduction of large amounts of mineral dust into the atmosphere and for their long range transport over the Mediterranean, Europe, North Atlantic Ocean and South America [2–5]. Sahara Desert is responsible for almost half of all the aeolian material transported to the world's oceans [6, 7], being considered the most important source of mineral dust [1, 4].

The atmosphere of Cape Verde is deeply marked by the contribution of this dust emission source since these islands are under the pathway of trade winds that transport dust from North African sources to the northern tropical Atlantic Ocean. At local level, the native population recognizes the importance of the Sahara influence, occurring mainly in the dry season, which is identified by “*bruma seca*” (dry smog), and characterized by high concentrations of airborne particulate matter from October to March.

It is well-known that the exposure to particles increases the occurrence of adverse human health effects [7]. Moreover, several studies revealed an increase not only on adverse respiratory syndromes, but also on the daily mortality rate during Saharan dust events [8–10]. Additionally, several investigators demonstrated that PM-induced

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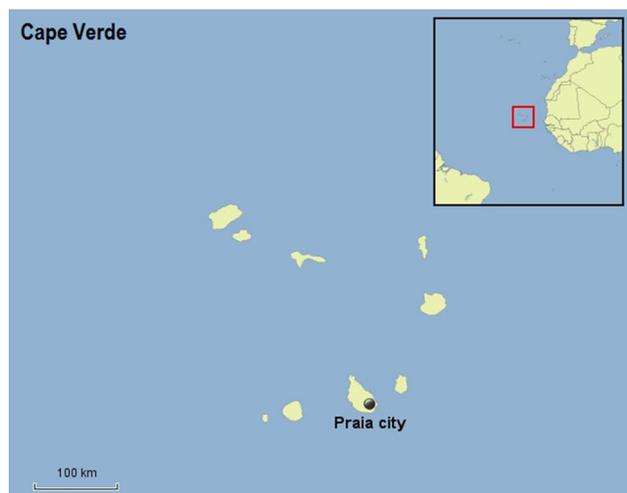


Fig. 1 Geographical localization of the Cape Verde islands

adverse human health effects depend not only on PM mass concentration, but also on its chemical composition [11].

PIXE and k_0 -INAA are two non-destructive techniques suitable to perform a multi-elemental analysis of air particulate matter. Several studies have already proved the effectiveness and the advantages of using both techniques for the multi-elemental characterization of air particulate matter [12–15].

The objective of this study was to characterize the aerosol from Cape Verde and to assess the influence of Sahara Desert dust on the composition of local suspended particles. This study was performed within the project CV-Dust—atmospheric aerosol in Cape Verde region: seasonal evaluation of composition, sources and transport—which aims to assess the transport of dust from Sahara Desert by using an integration of different measuring and modelling tools.

Experimental

PM₁₀ sampling

This study was carried out in Santiago's island, the biggest island of Cape Verde archipelago, which is composed by ten islands, located offshore of Western Africa coast. Santiago's island has an area of 991 km² (Fig. 1), and more than 200,000 inhabitants. It is localized directly in the route of Saharan dust transport to the Atlantic Ocean, being an ideal place to quantify and to characterize the African aeolian aerosol.

One Echo TCR Tecora sampler [16]—which is a low-volume particle sampler operating at an average flow rate of 16.3 L min⁻¹—was installed in Praia city (14°N; 23°49'W) during the year 2011. The sampler collected particulate matter with an aerodynamic diameter smaller than 10 μm (PM₁₀), on Nuclepore[®] polycarbonate filters

with a diameter of 47 mm, in a total of 140 samples. The sampling time ranged between 6 and 96 h, the shorter times being used during Saharan dust episodes. Therefore, the average values presented in this work were pondered according to the sampled volume.

The collected filters were weighted using a Mettler[®] Toledo balance with 0.1 μg readability. The balance was placed in a controlled clean room (class 10,000) at temperature of 20 °C and relative humidity of 50 %. Before weighing, the filters were equilibrated during 24 h in the same room (EN12341:1998). Filters were weighted before and after sampling and the mass was obtained as the average of three measurements, when observed variations were less than 5 μg.

Elemental analysis using k_0 -INAA

One quarter of the filters was rolled up, put into aluminium foils and irradiated at the Portuguese research reactor (RPI; nominal power: 1 MW) [17] for 5 h. After irradiation, the filters were removed from the aluminium foils and were inserted in polyethylene containers. Samples were measured for 5–7 h after 2–5 days and 4 weeks of decay using a high-resolution HPGe detector, associated with an ORTEC[®] automatic sample changer. A comparator—Al-0.1 % Au alloy disk with a thickness of 125 μm and a diameter of 0.5 cm—was co-irradiated with the samples for the application of the k_0 -INAA methodology [18]. The set of elements determined by k_0 -INAA were: As, Ba, Ce, Co, Cr, Fe, K, Na, Rb, Sb, Sc, Sm, and Zn.

Quality control was pursued by the use of the NIST-SRM[®] 1633a—Coal Fly Ash certified reference material. Approximately 50 mg of reference material was co-irradiated with each batch of samples and measured for 60 min after 2–5 days and 4 weeks of decay using the same detector.

Elemental analysis using PIXE

PIXE analysis was carried out at a Van de Graaff accelerator, in a vacuum set-up. Two X-ray spectra were taken for each of the samples: one with a 1.25 MeV proton beam and no absorber in front of the Si(Li) detector for quantification of low-energy X-ray elements and another with a 2.15 MeV proton beam and a 250 μm Mylar[®] X-ray filter to determine elements with atomic number higher than 20. The beam area at the target was 20 mm² [19]. The set of elements determined by PIXE were: Br, Ca, Cl, Cu, Mg, Mn, Ni, S, Si, Ti, V, and Pb.

Backward trajectories, cluster and statistical analysis

The NOAA/ARL HYSPLIT Model (HYbrid Single-Particle Lagrangian Integrated Trajectory) version 4.9 [20] was

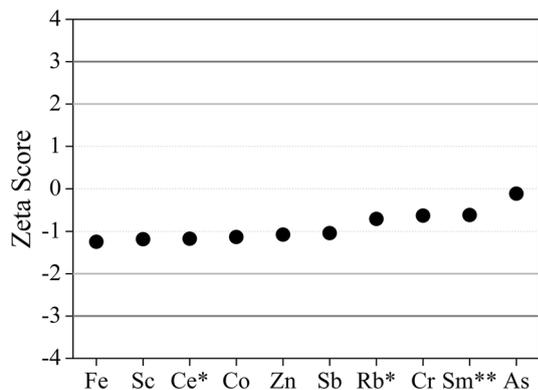


Fig. 2 Plot of Zeta-scores calculated for NIST-SRM[®] 1633a “Coal Fly Ash”. Asterisk indicative values and double Asterisk consensual values

used to determine three-day backward trajectories, ending in Santiago Island. The software was run for each sample at 1,000 m height, and using the vertical velocity option. A total of 140 trajectories were created, all considering the start time of each sampled filter. A cluster analysis was performed in order to assemble all backward trajectories according to its characteristics.

Statistical calculations were performed by Statistica[®] software. The analysis of the results variance was performed by nonparametric statistic for a significance level of 0.05: the Mann–Whitney U Test for binary independent groups.

Results and discussion

Quality control and quality assurance

The certified reference material NIST SRM 1633a Coal Fly Ash was co-irradiated with all batches of samples for quality control. The quality of the results was assessed by calculating the Zeta (ζ) scores for the certified reference material. The certified values were used according to the NIST certificate and also the indicative and consensual values provided by Roelandts and Gladney [21]. Figure 2 shows that all elements yielded Zeta-scores within a good agreement (between 2 and -2) [22].

Agreement between PIXE and k_0 -INAA for the elements Zn, K and Fe (measured by both techniques) was evaluated and results are presented in Fig. 3. For K and Fe a very good correlation between techniques was obtained ($r^2 = 0.96$ for K and $r^2 = 0.94$ for Fe). For Zn a lower correlation coefficient was obtained probably due to the fact that this element is present at lower concentrations, and consequently its distribution on the filters is more heterogeneous [14, 23]. A detailed discussion on this and

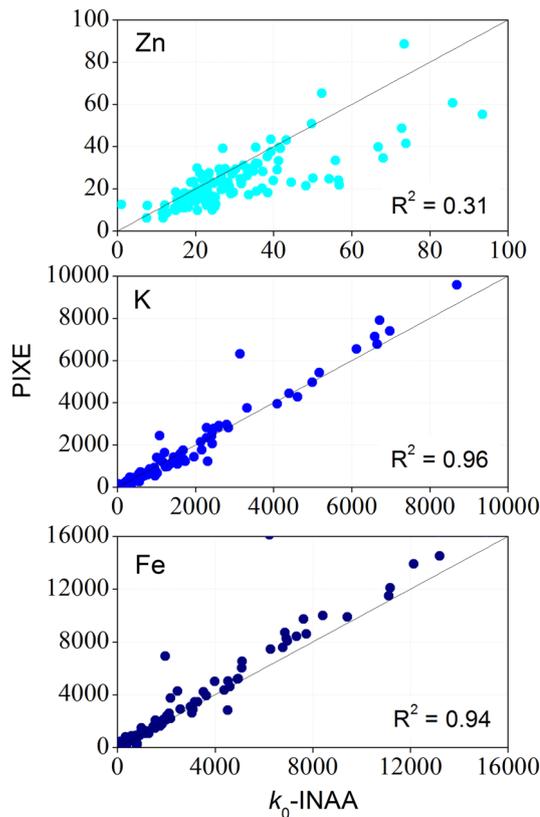


Fig. 3 Correlation between PIXE and k_0 -INAA for Zn, K, and Fe. Results are presented in ng m^{-3}

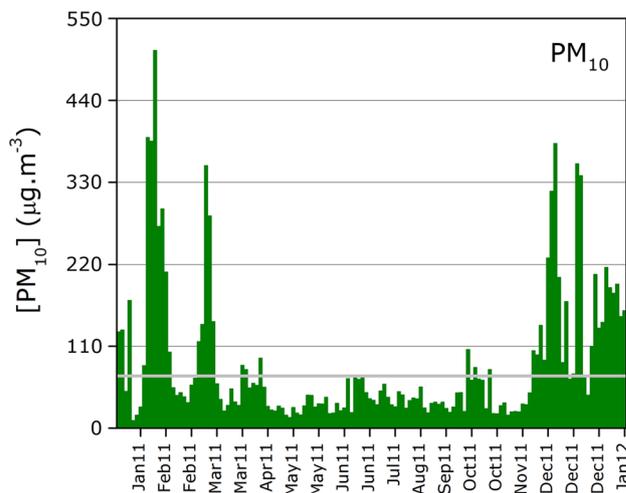


Fig. 4 Seasonal variation of PM_{10} mass concentration. The grey line shows the average value and the results are presented in $\mu\text{g m}^{-3}$

related issues has been presented elsewhere [23]. Therefore, k_0 -INAA concentrations were used for these elements because a larger part of the filter is analysed by this technique, which makes the analysis result more representative.

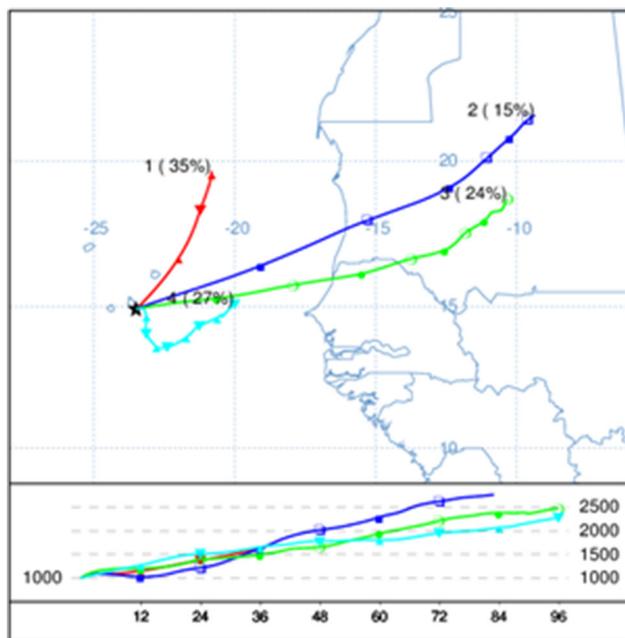


Fig. 5 Cluster analysis obtained by backward trajectories calculated with Hysplit Model

PM₁₀ concentration

Figure 4 presents the seasonal variation of PM₁₀ concentration measured during the sampling campaign. The PM₁₀ average concentration was $56 \mu\text{g m}^{-3}$. This value exceeded all the annual standard international guidelines: $20 \mu\text{g m}^{-3}$ defined by World Health Organization [24]; $40 \mu\text{g m}^{-3}$ defined by the European Directive 2008/50/EC [25]; and $50 \mu\text{g m}^{-3}$ defined by U.S. European Protection Agency [26].

The variability throughout the studied year shows the existence of a pattern: higher PM₁₀ concentrations from December to March and lower values during the rest of the year. The period between November and March is defined as a dry season and is typically named *Harmattan* [27]. In fact, this behaviour is in line with different studies that showed higher concentration of PM₁₀ during this period [28]. For instance, Goudie and Middleton [6] referred that in the south of the Sahara Desert the higher number of days with blowing dust/sand occur between November and March [7]; and in a study developed in Canary Islands the total suspended particles reached the concentration of $5,586 \mu\text{g m}^{-3}$ during the dry season [28].

PM₁₀ elemental composition

The application of the cluster analysis to the backward trajectories identified four groups presented in Fig. 5. These four clusters showed the existence of two different trends: (a) clusters 2 and 3 are clearly associated with air

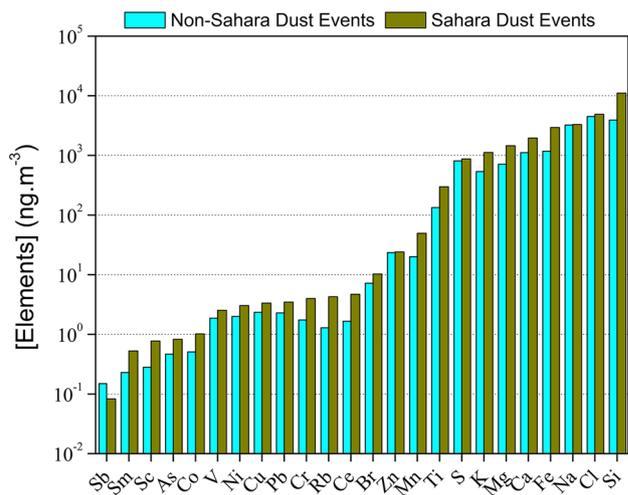


Fig. 6 Elemental composition of PM₁₀ from Cape Verde during Sahara Desert dust events and Non-Sahara Desert dust events

mass trajectories coming from Sahara Desert and (b) clusters 1 and 4 represent trajectories without a Sahara origin. Considering this, the PM₁₀ elemental composition was discriminated by these two trends: “non-Sahara Desert dust events” and “Sahara Desert dust events”.

Figure 6 shows the elemental composition from Cape Verde during both events. As a first approach the chemical element concentrations were sorted from the lowest to the highest value. The results obtained are in line with a previously study [29], presenting high levels of elements originated from the soil (Ca, Ce, Co, Fe, K, Mg, Mn, Rb, S, Sc, Si, Sm, and Ti) and low concentrations of anthropogenic elements (As, Cr, Cu, Ni, Pb, Sb, V, and Zn). Sb and Zn exhibit a different behaviour compared with the other elements, because their concentrations did not show significant differences between both events (Sb: p value = 0.41; Zn: p value = 0.1). Moreover, Sb and Zn did not give a good correlation with PM₁₀, in both periods (Fig. 7). Other anthropogenic elements, such as Br, Cu, Ni, Pb and V, presented not only significantly higher concentrations during Sahara dust events but also good correlations with PM₁₀ during these periods ($r^2 = 0.44$; 0.62 ; 0.81 ; 0.71 and 0.48 , respectively).

The elements commonly associated with soil—Ca, Ce, Co, Fe, K, Mg, Mn, Rb, S, Sc, Si, Sm and Ti—had significantly higher concentrations during the “Sahara Desert dust events” (p values < 0.05), as observed in other studies [29–31]. The ratio between Sahara Desert dust events and Non-Sahara Desert dust events for each soil element was higher than 2 for Ce, Cr, Fe, K, Mg, Mn, Sc, Si, Sm and Ti; and higher than 3 in the specific case of Rb. As it is possible to observe in Fig. 7 the correlation between PM₁₀ and those elements was very good, yielding r^2 of 0.94, 0.69, 0.96, 0.81, 0.96, 0.64, 0.96, 0.92, 0.92, 0.94, respectively, and 0.81 for Rb.

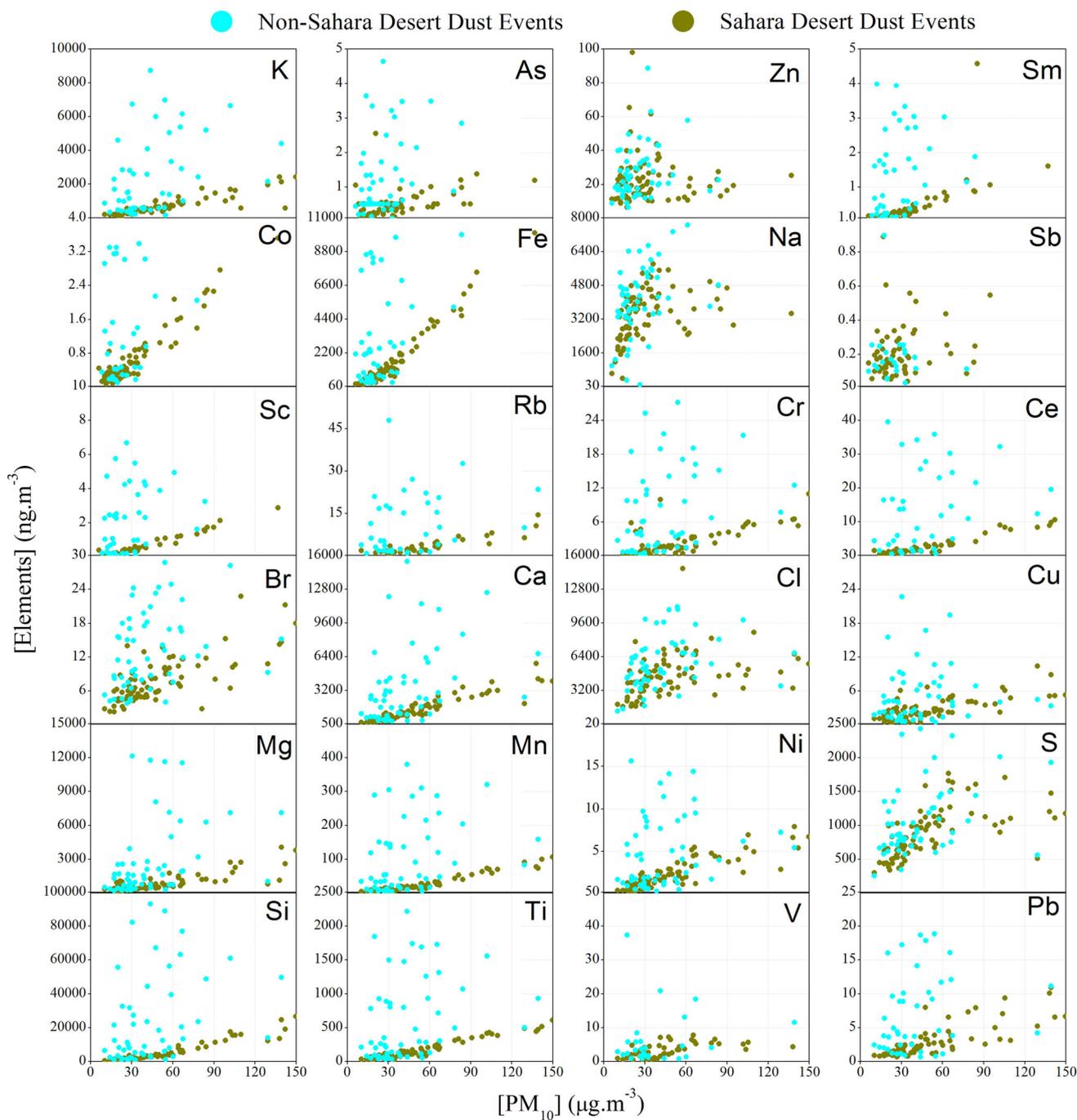


Fig. 7 Correlation between PM_{10} and chemical elements obtained during Sahara Desert dust events and Non-Sahara Desert dust events

These results showed that during the Sahara Desert dust events there was an increase not only of PM_{10} total mass concentrations and crustal elements, but also of anthropogenic elements.

Due to Cape Verde geographical position, sea salt contribution was significant in all samples, irrespective of air mass origin. The ratio between Sahara Desert dust events and Non-Sahara Desert dust events for Na and Cl was 1.02 and 1.09, respectively.

Figure 8 compares the concentrations obtained in this study with results obtained at other sites of the globe [32–54]. The results showed that PM_{10} levels in Cape Verde were higher than concentrations measured in Europe and America [32–45], but lower than the concentrations measured in a suburban area in Ghana [46]; in Agra (India), in the vicinity of the Thar Desert of Rajasthan [47]; and in Hangzhou that is an industrialized and urbanized region [48]. A similar behaviour was found for Fe. Since this

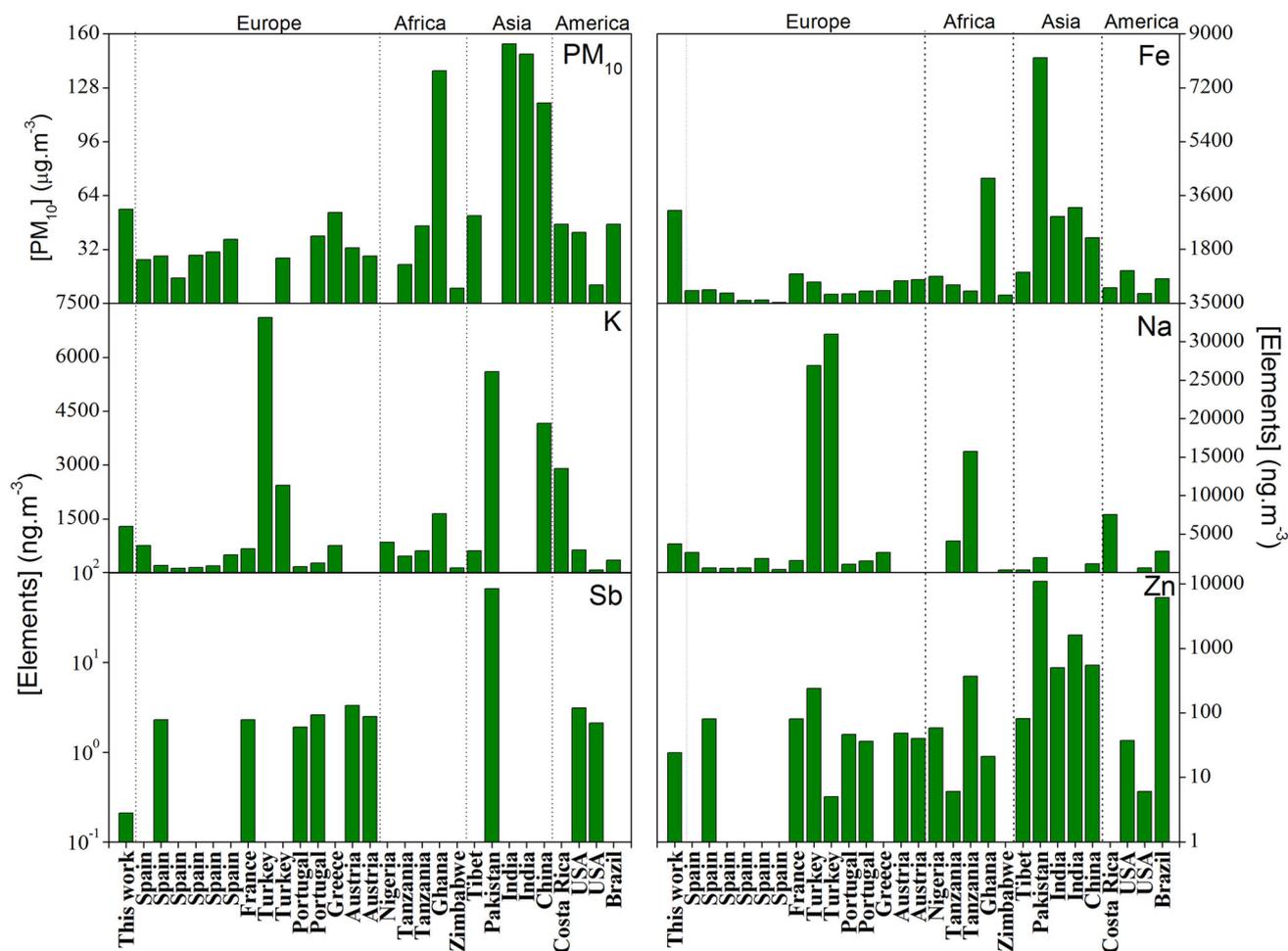


Fig. 8 Average concentrations of PM_{10} and chemical elements in different sites of the World

element is commonly associated with soil, the highest concentrations were registered in sites characterized by dry climates and in urban areas where re-suspension of the road dust is a significant source. Sodium concentrations in Cape Verde presented the highest concentrations, this fact being concordant with the geographical position of the island. Potassium concentrations were higher in Cape Verde compared with concentrations measured in Europe and America but lower than concentrations measured in Pakistan, Ghana, and China [47–49]. Almeida et al. [50] demonstrated that this element is associated with soil (insoluble coarse fraction), sea (soluble coarse fraction), and combustion (fine fraction), being a common tracer of biomass burning [55]. The higher concentrations of this element measured in the Cape Verde are explained by the fact that the natural sources (soil and sea) are predominant in the island. The probable influence of the biomass burning from the African Continent needs to be studied further. For the elements As, Sb, and Zn an opposite behaviour was observed with lower concentrations in Cape Verde compared with other referred sites. These elements

are associated with anthropogenic sources, as combustion processes, vehicle exhaust, and industrial processes [29, 56, 57].

Conclusions

The current study aimed to characterize the Cape Verde aerosol and to understand the possible influence of Sahara Desert dust events on its characteristics.

PM_{10} mass concentrations exhibited seasonal variations, characterized by higher levels in the dry season. In 2011, the PM_{10} health-based air quality guidelines defined by WHO, EU, and USEPA were exceeded.

The k_0 -INAA and PIXE elemental characterization of particles indicated a strong influence of the Sahara Desert dust events upon Cape Verde aerosol. The comparison between events and the correlation between PM_{10} and the chemical elements indicated that during these periods higher concentrations of both mineral and anthropogenic elements were observed.

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