Aerosols metal solubility and trace metal composition in marine aerosols at CVAO

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Surface Ocean Processes in the Anthropocene

Introduction and Motivation

Trace elements are important mineral nutrient in the Oceans. They play an important role in the oceanic ecosystem thereby influencing the global carbon cycle. Iron is a very important metal in the oceans since its presence influences phytoplankton growth thereby influencing the marine biota. Although iron is important, the main flux is the bioavailable iron which is readily accessible for marine organism.

In the region of the tropical northern Atlantic, Saharan dust constitute one of the major source of these nutrients into the ocean. However, iron in Saharan dust is not very soluble, but could be significantly modified after long range transportation by atmospheric processes.

At CVAO (Fig 1) we have monitored the aerosol trace metal solubility in order to improve our understanding of which atmospheric processes control the metal solubility and in which chemical redox state are the metals present. Here, we report on the results of trace metal solubility of marine aerosol particles during a three intensive field studies lasting for 4-6 weeks predominantly during the dusty winter seasons of 2010, 2011 and 2012. Figure 2 shows the typical air mass footprints at CVAO.

Sampling Site

Fig. 1: *Cape Verde Atmospheric Observatory (CVAO) with a 30 m-tower for Aerosol particle sampling , ~100 m offshore.*

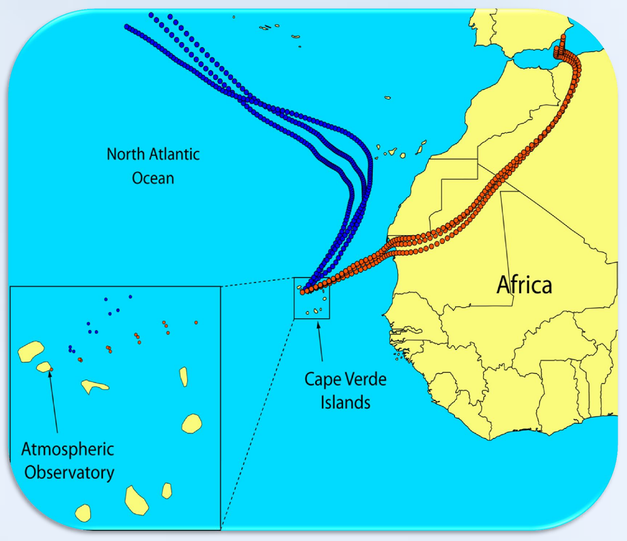

Fig. 2*: Cape Verde Islands situated on the west cost of Africa and the CVAO located at the Island São Vicente. Blue and orange back trajectories represents air mass origin during low and high dust periods, respectively.*

Experiment and Sampling

Aerosol particle sampling has been done at the top of a 30 m tower. For the analysis of soluble metals a low volume sampler (4 m³/h, PM_{10}-inlet) was routinely operated every 24 h on 47 mm teflon filters. The filters were analyzed for water soluble metals including Fe (III), Fe (II), Cu (II) , Zn (II) and Mn (II) using an ion chromatography.

A five-stage BERNER impactor with a PM_{10} cutoff (0.05-10 µm size range) was operated in a 24 h sampling interval, collecting size-resolved samples on aluminum and nuclepore foils. The nuclepore foils were used to characterize the total trace metal content, using a Total Reflection X-ray fluorescence (TXRF) technique. The picture of the two collectors are shown in Fig. 3.

Fig. 3: *a) Derenda low volume sampler with PM_{10}-inlet, with 4 m³/h sampling rate on 47mm teflon filters*
b) 5 -stages BERNER impactor with 75 l min^{-1}, sampling rate on aluminium and Nuclepore® foil (Wicom Heppenheim GmbH, Germany), stages lower cut-offs:
0.05 - 0.14 - 0.42 - 1.2 - 3.5 -10 µm.

Results

The trace metal concentration was found to be strongly correlated with the Saharan dust storms. The highest concentrations were observed in the winter seasons. The trace metals of crustal origin including, Fe, Ca, Ti, Mn, Si, A were mostly found in the coarse mode as shown on figure 4 for the case of Fe.

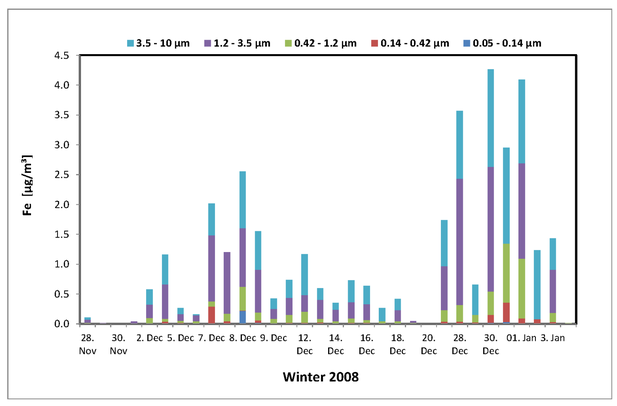

Fig. 4 *Trace metal size distribution showing crustal metals in mostly coarse mode as illustrated with iron.*

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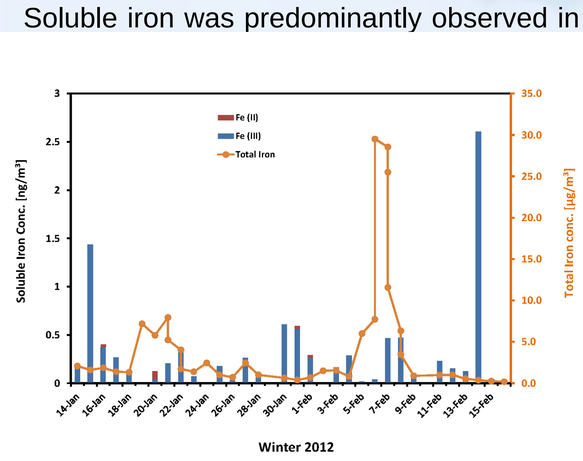

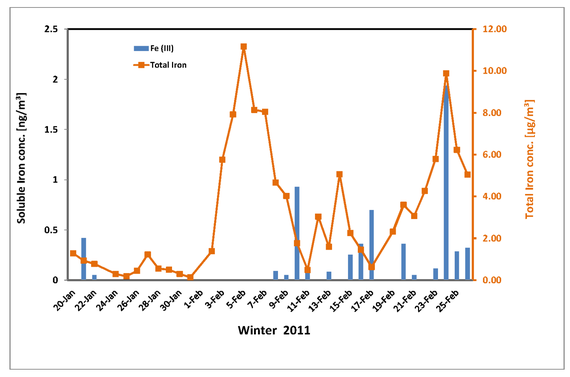

centrations low 6a) and high dust events 6b) from BERNER samples (2007).

OC and EC were found in very low concentrations except during dust events where the concentration increase by about a factor of five due to the influence of air masses from the African continent. As expected, the mineral dust proportion of the PM_{10} mass increased significantly during dust events and constituted to more than half of the particulate matter especially in the coarse mode.

During periods of high dust concentrations the majority of the particulate matter came from the Sahara with a high composition of crustal metal (see orange trajectories in Fig. 2). As shown on Fig. 5, a linear correlation between the measured iron content and the total sampled PM_{10} mass shows a high content of crustal materials in the particles. A similar correlation was also found for other crustal metals such as Ca and Ti.

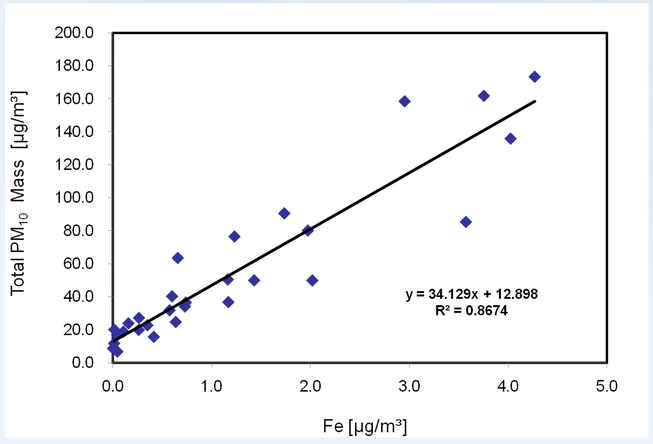

Fig. 5. *Linear correlation between measured iron and total PM_{10} mass concentrations, shows that the PM_{10} mass are of crustal origin.*

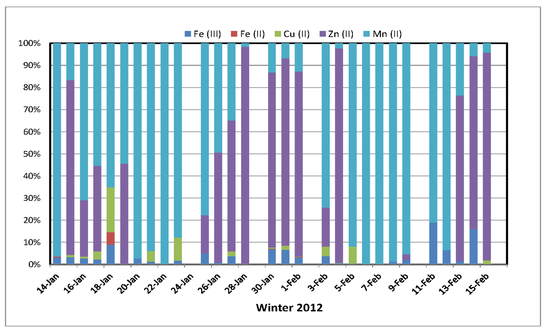

Fig. 7: Average composition of trace metals observed during a dust event from BERNER samples.

With the exception of aluminum and silicon; iron, calcium and titanium were the dominant crustal metals observed with mass concentrations of about 4.2 (Fe), 3.4 (Ca), 0.3 (Ti), and 0.1 µg/m³ (Mn) in comparison to concentrations of less than 1.0 ng/m³ during days with low dust and mostly marine influenced activities. Fig. 7 shows the average percentage composition of Ca, Fe, Ti, Ni, Cu, Zn, Cr, Sr, V, Mn, Co and Pb during a dust episode.

Summary and Outlook

The results of the particle analysis show a distinction between dust and low dust events. Most high dust events occur during the winter months with elevated mass concentrations in the coarse mode. Air masses during dust events originated mostly from the African continent with air masses traveling through the Saharan desert. During dust events, the crustal materials made up more than 60% of the PM_{10} mass. The mean crustal metal concentrations observed were about 4.2 (Fe), 3.4 (Ca), 0.3 (Ti), and 0.1 (Mn) µg/m³.

Acknowledgement

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