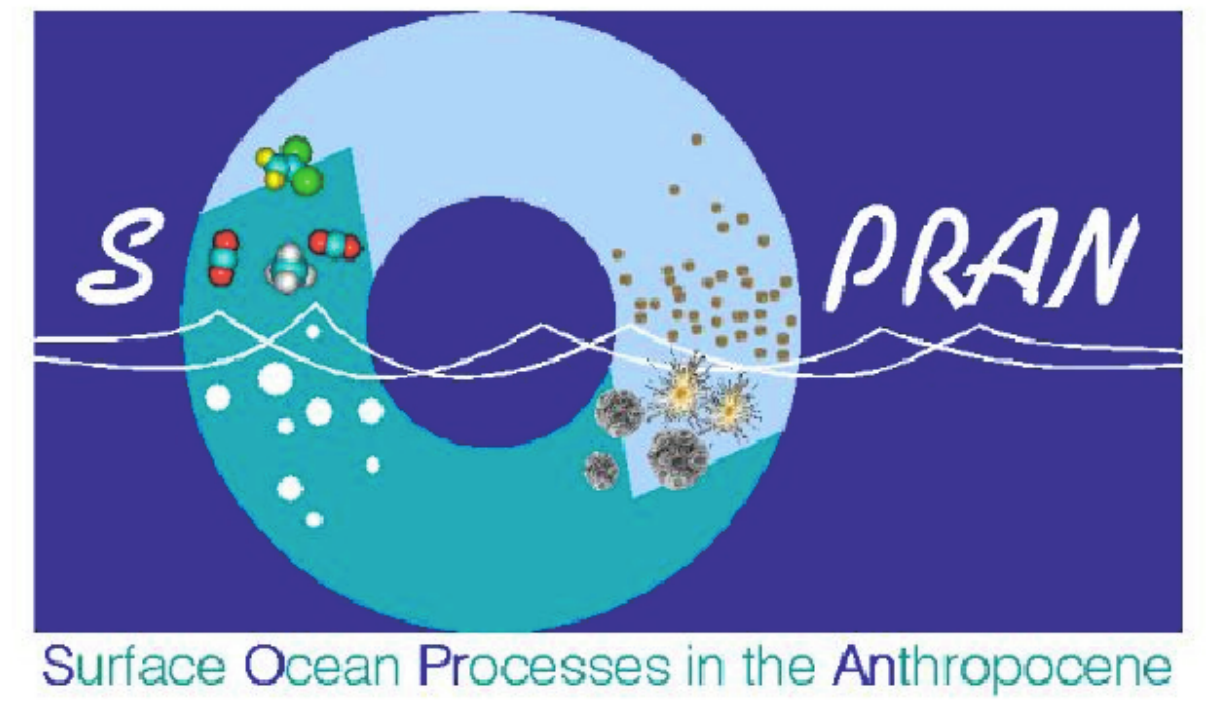


Aerosol metal solubility and trace metal composition in marine aerosols at CVAO



Khanneh Wadinga Fomba, Konrad Müller and Hartmut Herrmann

Leibniz-Institut für Troposphärenforschung, Permoserstr. 15, D-04318 Leipzig, Germany
fomba@tropos.de



Introduction

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 that may also lead to a change of its oxidation state.

At CVAO (Fig. 1) we have monitored the aerosol trace metal solubility in order to improve our understanding of the atmospheric processes that control aerosol metal solubility and in which chemical redox state they are 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 2008, 2011 and 2012. Figure 2 shows the typical air mass footprints at observed at CVAO.

Sampling Site



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

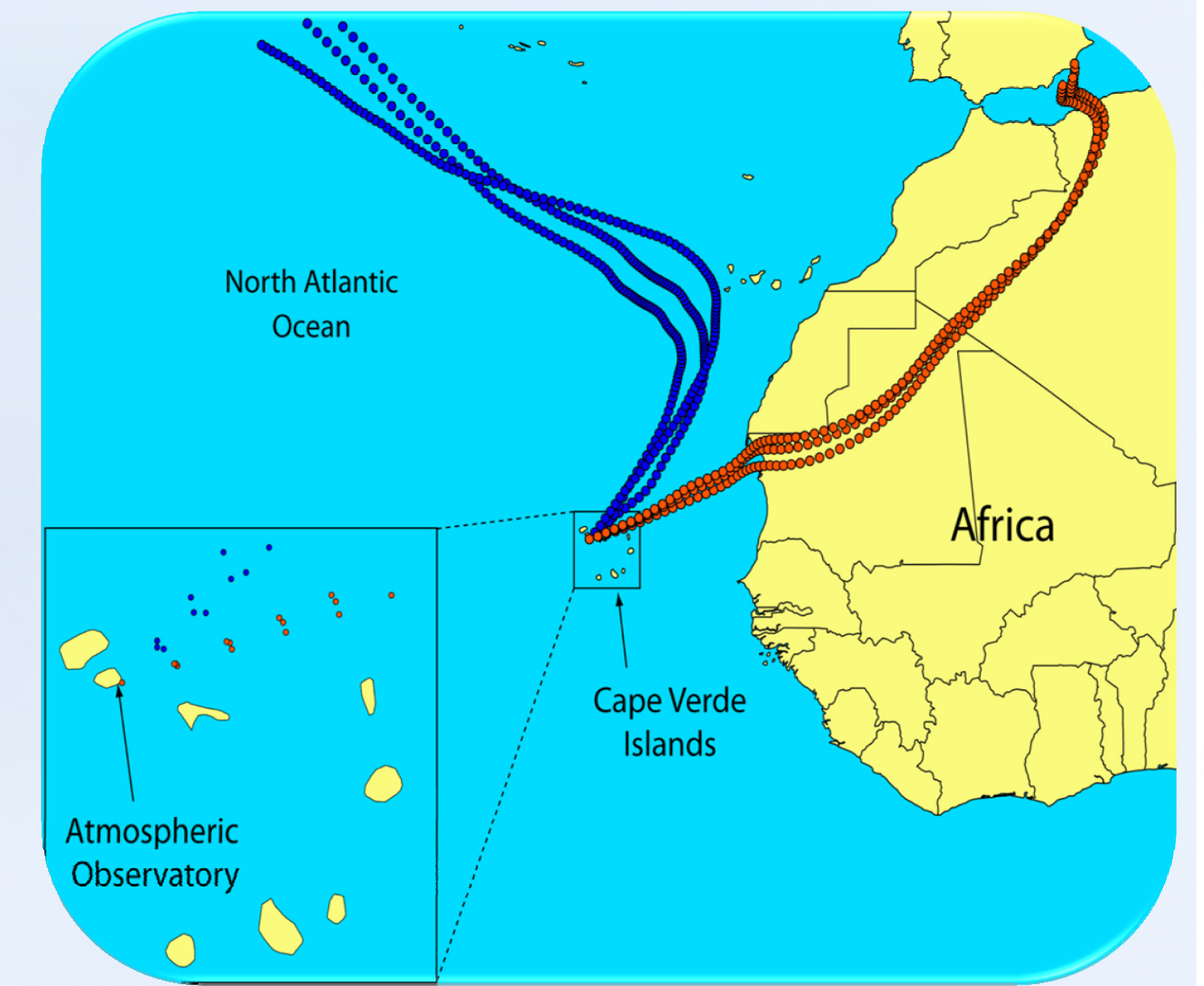


Fig. 2: Cape Verde Islands situated on the west coast of Africa and the CVAO located at the Island São Vicente. Blue and orange back trajectories represents air mass origin during low and high dust periods, respectively.

Experiment and Sampling

Aerosol particle sampling has been done at the top of a 30 m tower. A low volume sampler (4 m³/h, PM₁₀-inlet, Fig. 3a) was routinely operated every 24 h on 47 mm Teflon filters. The filters were leached with DI water (pH 5.5) via shaking for 2 hours and were analyzed for water soluble metals including Fe (III), Fe (II), Cu (II), Zn (II) and Mn (II) using an IC.

A five-stage BERNER impactor (Fig. 3b) with a PM₁₀ 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.



Fig. 3: a) Derenda low volume sampler with PM₁₀-inlet, with 4 m³/h sampling rate on 47mm Teflon filters b) 5-stages BERNER impactor with 75 l min⁻¹, sampling rate on aluminum 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 concentrations were found to be strongly correlated with the Saharan dust storms. The highest concentrations were observed in the winter seasons (Müller *et al.*, 2010). The trace metals of crustal origin including, Fe, Ca, Ti, Mn, Si, Al were mostly found in the coarse mode PM as shown in figure 4 for the case of Fe.

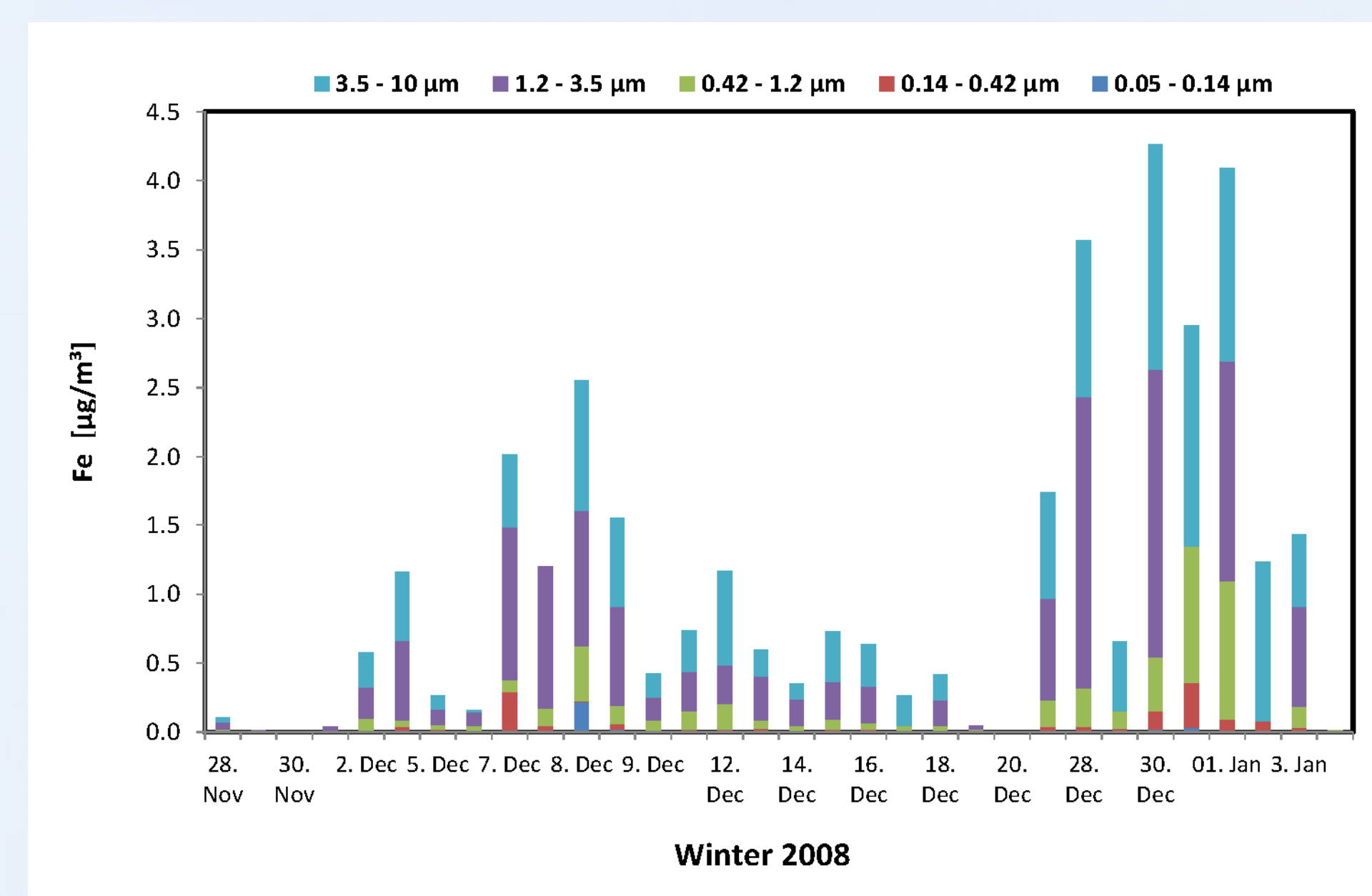


Fig. 4 Trace metal size distribution showing crustal metals in mostly coarse mode PM as illustrated with iron.

During periods of high dust concentrations the majority of the particulate matter came from the Sahara with a high composition of crustal metals (see orange trajectories in Fig. 2). As shown on Fig. 5, the good correlation between total iron and the total sampled PM₁₀ mass concentrations indicates that the observed metals were of crustal origin (Carpenter *et al.*, 2011). A similar correlation was also found for other crustal metals such as Ca, Ti and Mn.

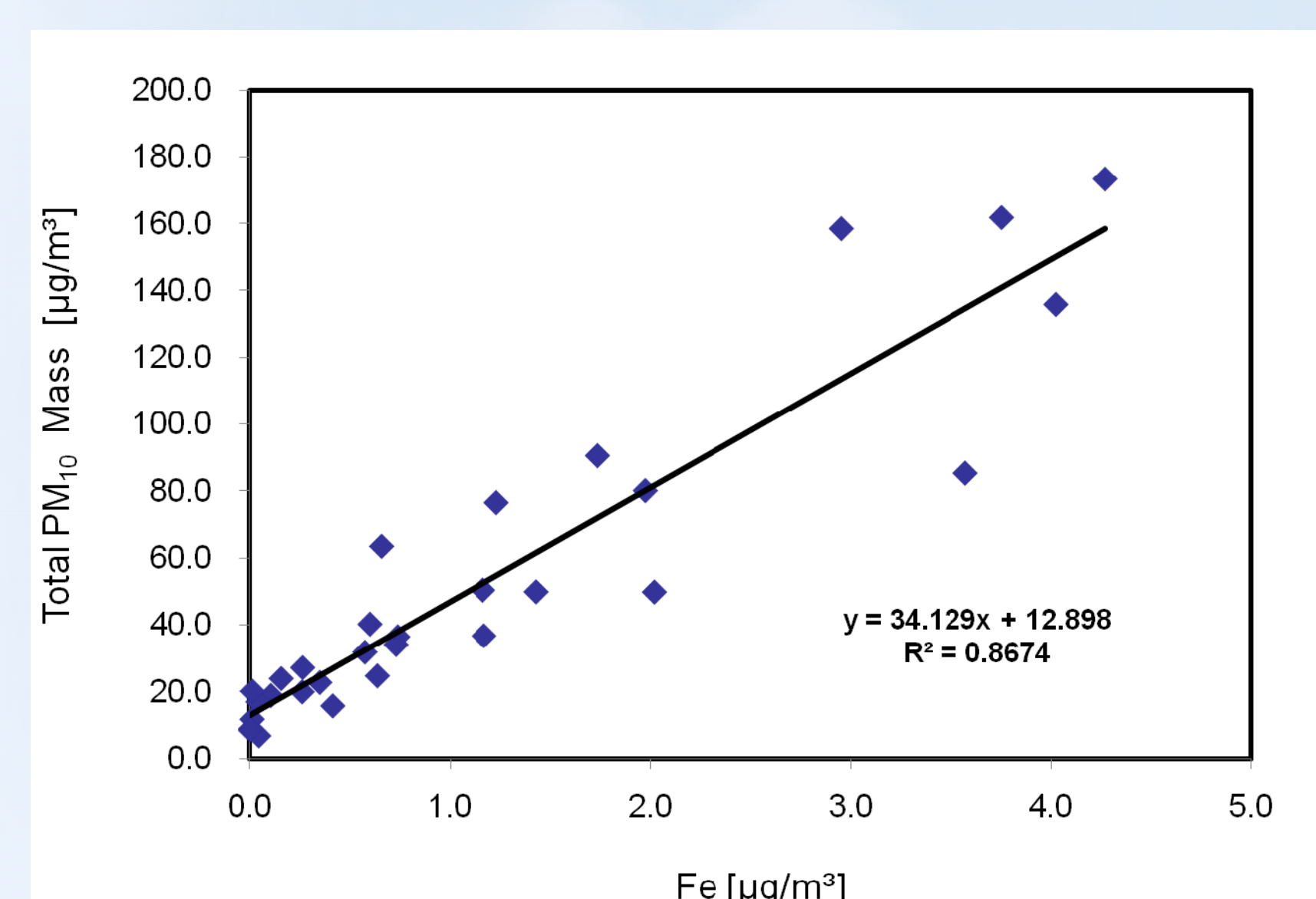


Fig. 5. Linear correlation between measured iron and total PM₁₀ mass concentrations, shows that the iron is mainly of crustal origin.

Water soluble iron was predominantly observed in the iron (III) state during the winter campaigns. The total iron concentrations showed more or less an anti-correlation with the water soluble iron concentrations with days of higher iron concentration yielding mostly lower water soluble iron. Figures 6 shows a similar trend in behavior for both 2011 and 2012, with higher iron loadings and soluble iron (II) observed in 2012 as compared to 2011.

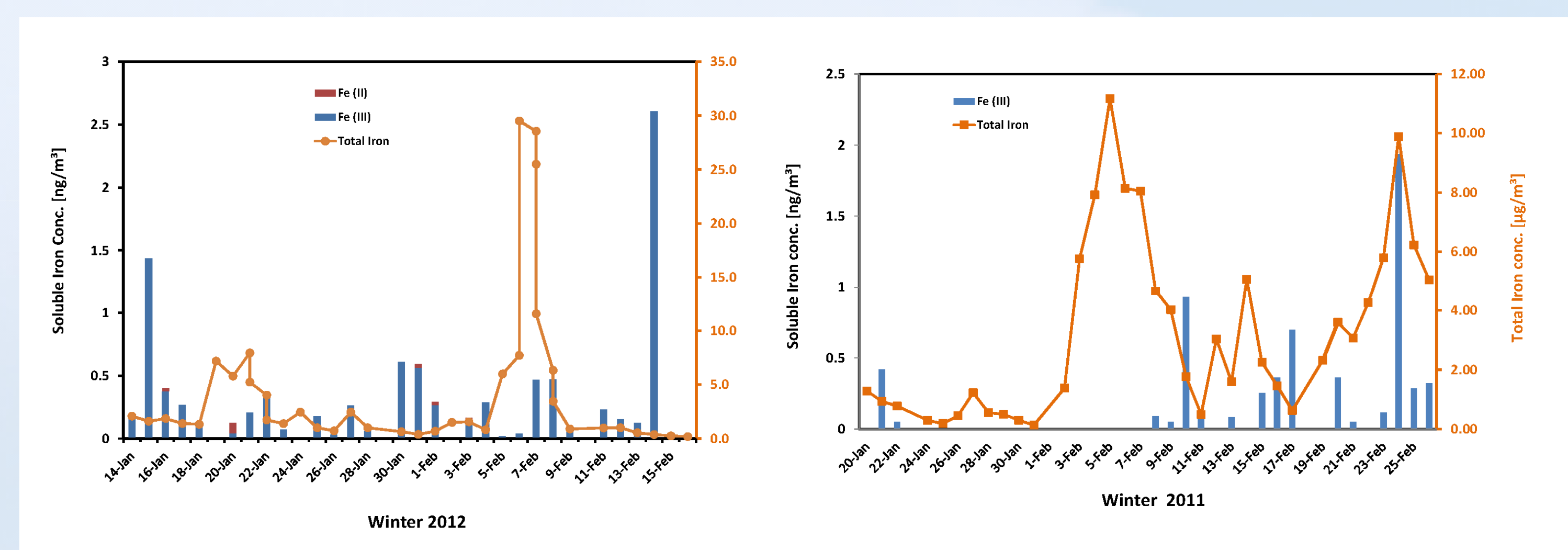


Fig. 6: Total and water soluble iron concentrations during two winter campaigns showing lower iron solubility during dust events.

Amongst the measured soluble metals, Mn (II) and Zn (II) were more soluble than iron. For both campaigns, Mn solubility was far above 5 % and was mostly observed in Mn (II) state. Days with high zinc solubility were correlated with days of mixed aerosol with greyish brown filters, indicating that the air mass contained almost the same contribution of both anthropogenic emissions and Saharan dust.

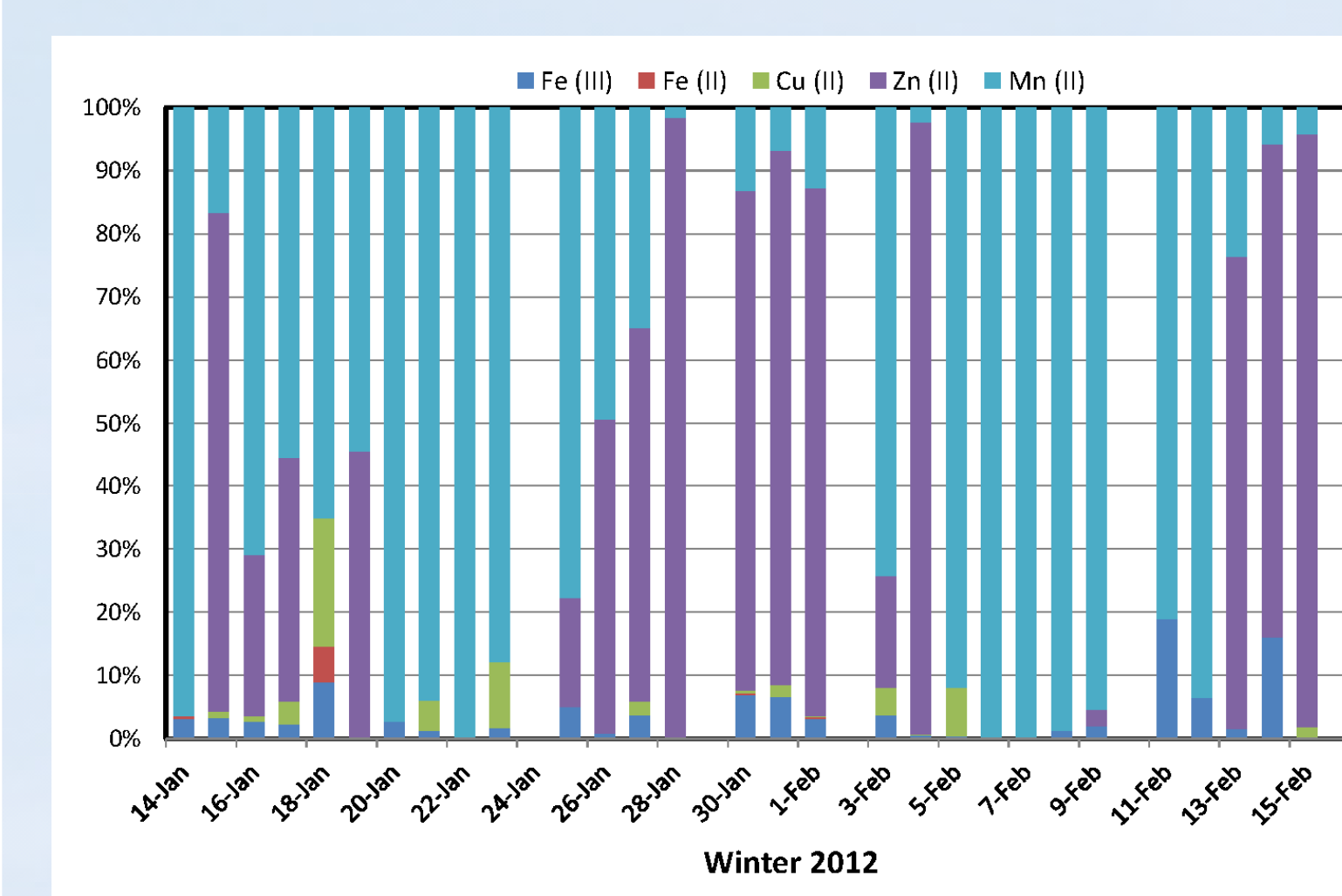


Fig. 7: Relative composition of water soluble metal ions showing a higher Mn and Zn solubility through out the campaign.

Summary

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. Water soluble iron concentrations do not correlate with high dust loadings while Mn and Zn were found to be more soluble than iron. Higher aerosol metal solubility was observed only at low pH's.

Acknowledgement

This work was supported by the German Federal Ministry of Education and Research (BMBF) within the SOPAN project

References

Müller, K. *et al.*, *Atmos. Chem. Phys.*, **2010**, 10,1-13.
Carpenter, L. *et al.*, *J. Atmos. Chem.*, **2010**, 67:87-140