Interactive comment on “Aerosol size-resolved trace metal composition in remote northern tropical Atlantic marine environment: case study Cape Verde Islands” by K. W. Fomba et al.

Anonymous Referee #1

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Review of Fomba et al., This manuscript describes a very comprehensive set of measurements of total trace metal concentrations in aerosols collected at the Cape Verde Atmospheric Observatory. The concentrations of such a large suite of trace metals in aerosols have not been reported previously from this site and the quality and scale of this data set certainly merits publication. However, I would suggest some modifications to the paper prior to publication.

1. Introduction Line 25 There are I think two primary seasons of dust transport to the Atlantic, although one of these is at high level and has rather little impact on Cape Verde. Nevertheless it would be useful to clarify this. Also generally the utility of considering mass concentration of aerosol may be limited. The authors do not present sea salt data, but it will inevitably be present at relatively high concentrations. Hence unless the authors provide sea salt data to demonstrate that aerosol mass is related to dust loading, I would suggest eliminating the discussion of mass loading.

2.2 Methods XRF analysis is not widely used for aerosol analysis so I would suggest that the authors clarify a few details of the methods. Firstly explain about the “spots on the foils”. Then explain “spots were placed on substrates” and why acid was added. As the authors note the “spots” seem to be the same size as the XRF beam, so confirmation that the whole of the sample is analysed is required. What reference materials beside the internal Ga standard were analysed? Line 24 what does “were not probed” mean, I assume the blanks were deployed with no air sucked through them, but the text is ambiguous.

2.3 Back trajectories The authors should explain rationale for the complex procedure they have undertaken to create 648 trajectories to describe each sample. This approach no doubt provides a very good characterisation of the air parcel's possible transport, but why was this done and does it yield a much better estimate than using just a few trajectories?. I did not really understand the way that this information was merged with geographical data. The text suggests that landscape types had different colours - are these the colours in Fig 3? It seems inevitable that all samples at Cape Verde will have had a marine trajectory before arrival and the other classification into urban or agricultural areas seems at such a small scale that I cannot actually see it in Fig 3. Clearly a terrestrial versus exclusively marine trajectory is useful, as is differentiating between Europe and North America but, given the uncertainties in 4 day back-trajectories, I wonder about the value of subdividing landscape types beyond perhaps identifying the deserts. I note in the van Pinxteren et al reference cited this approach was used for urban source apportionment where I can readily understand it's utility, but it would be useful for the authors to indicate the way this high resolution source location improved their analysis for Cape Verde samples.
3.1 Aerosol mass concentration In the discussion of the mass concentrations and wind speed relationship for remote samples, it would be useful to know if the increase in mass at higher wind speed is simply related to higher sea salt concentrations.

3.2 Air mass analysis It is a rather pedantic point, but in the trajectory classes, even the SS, SU and EA classes must surely include an element of marine.

3.3 Trace metal concentrations I would suggest that having measured the concentrations in all the samples, the authors should include all the data including the “non remote” trajectory regions, even if they then choose to focus on the remote samples. The results can simply be tabulated. Their data base will be valuable to other workers. Para 2 I accept the point that Marine North American air masses may be highly variable. This seems to me likely to reflect the air masses passing over high or low emission areas and/or at high or low altitudes. If the authors believe the explanation relates to wind speed as stated here, they should explain that further. The Weisel et al., 1984 paper does suggest quite large trace metals emissions from the oceans, but Hunter 1997 (in Sea Surface and Global Change eds Liss and Duce Cambridge Press) suggest a much weaker source. Much of the discussion in this section involves numeric comparisons to other data and I wonder if this might be simplified to a table. The general conclusion is that results are consistent with other data which is useful but could be said quite briefly. Comparisons to some of the SEAREX Pacific sites should at least note that those are considerably more remote than Cape Verde from terrestrial sources. There is a concluding sentence “Generally metals from crustal origin…” which I disagree with. Clearly metals from crustal sources will be higher in European air masses, the transit times from source regions are shorter and the European air masses pass close to arid source areas. However, I would suggest the authors statistically test if the Cu, Zn, Cr and Ni concentrations are higher in MNA air masses. I doubt from the data in Table 2 that this is true for Cr and Ni. It may be statistically true for Cu and Zn and if that is the case I think the authors might want to explore emission inventories to see if North American emissions are really high. The most recent compilation I know of (Pacyna 2001 Environ Rev 9 269-298) is of course from some years ago but it does not seem to suggest North American and European emissions are very different for these metals.

3.4 Size resolved analysis. I do not understand the point in this section about wind speed. Also the authors make much of the fine mode crustal metals, but the size differentiation is essentially statistical so I am not surprised that a percentage of crustal associated metals are in the fine mode (SEREX saw this many years ago e.g. Arimoto et al 1989 In Chemical Oceanography vol 10 ed R Duce). Similarly metals such as Cr, Ni Cu, Zn and Pb will condense to existing aerosols after gas phase emission and this will give them a dominantly fine mode distribution, but it will not be exclusive as again SEAREX showed. In the case of Pb the massive decline in emissions probably means that resuspension of contaminated soils may now be an important source. There is now evidence that marine colloids can be introduced to the atmosphere and could be a potential source of metals as the authors note, but in the absence of evidence such as from inter-element correlations the authors cannot demonstrate that this source is important compared to the well documented anthropogenic fine mode source. The importance of marine sources and their impact on aerosol Se are quite well documented (e.g. Arimoto et al., 1995 JGR 100, 1199-1213).

3.5 Enrichment Factors Ti is a perfectly suitable normalising element, but I do not understand the comment “iron has a wider origin in oceanic regions than titanium”. The authors here assume an EF outside the range 0.7-2 represents enrichment. Given the variability in crustal composition others have set an EF of 10 as a threshold (e.g Arimoto et al., 1989), so the authors may want to be cautious in interpreting relatively small EF values. The results here demonstrate that Fe has no enrichment and the authors might want to discuss this in relation to the argument that there is substantial emission of anthropogenic iron (e.g. Sholkovitz et al 2012 Geochim. Cosmochim. Acta 89, 173-189). The results here seem to suggest that anthropogenic iron is minor. A minor point in the discussion of “group iii” I do not understand the units for a Ni emission factor of
mg kg⁻¹, kg of what? And in the next sentence, “fly ash” is not an “activity”. It would be useful to test conclusions from enrichment factors against emission inventories such as those of Pacyna. The authors should perhaps note in the discussion of EF values that, for mixed source elements such as Mn, in dusty environments EF values will fall as the anthropogenic Mn is “diluted” with crustal material.

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