

Review of the manuscript “ Long-term chemical characterization of tropical and marine aerosols at the CVAO: field studies (2007 to 2011)”

This paper describes long term measurements of aerosol chemical composition in the marine environment of Cape Verde Atmospheric Observatory. It also shows the seasonal variations of different compounds and evaluates the influence of different air masses and sources. It derives a percentage contribution from dust and sea salt particles as well as long range transport. This is indeed a very exceptional data set and deserves a publication in ACP, however, some discrepancies should be corrected before the publication.

Consistency in the discussion should be kept throughout the paper, currently the conclusions made in one section contradict to the ones made from different measurements (secondary sulphate production is attributed to biogenic source in one place, and then it is connected to the anthropogenic source due to the correlation with nitrate. Chlorine/bromine depletion is calculated using all acids available without acknowledging any neutralization by ammonium; the large fraction of freshly emitted sea spray as shown by the PMF was also not accounted in the discussion on chlorine depletion. The same with organic matter, it is sometimes attributed to the marine source without any proof or discussion, while it could be the case, it should be clearly evaluated and discussed.

PMF source apportionment analysis. Factor selection criteria should be described as well as some statistical information provided. Information on factor solutions with higher and lower number of factors should be either presented or discussed. Uncertainty estimation method is described in the experimental section, but not discussed nor presented in the result section or figures. How the uncertainty differed for different number of factors?

How clean were the marine air masses, discussed here as “pure” marine air masses? What was the criterion? Provide EC/nitrate concentrations for the “pure” marine air masses. Moreover, chlorine depletion in these masses would still indicate an influence from anthropogenic source or do you imply that depletion by biogenic sulphuric acid occurred? For example, nitrate concentrations are quite high (as presented in table 5) for the marine air masses, were the same marine air masses were named as “pure” marine, or there were any other criterion?

Specific comments:

p. 3922, Lines 25-26: is 105°C enough to get rid of organics, please provide a reference to this methodology, as to my knowledge, higher temperatures are required to properly eliminate the background [Cavalli *et al.*, 2010].

p.3925, L3-17: reference to fig. 1 would help.

p.3926, L24-28: can you provide some error estimates associated with the water error, e.g. in dust quantification.

p.3927, L22-25: Define how you calculate nss-sulphate (e.g. in experimental section). If it comes from subtracting ss-SO<sub>4</sub> from the total SO<sub>4</sub>, how big the uncertainty would be for nss-

sulphate in marine PM<sub>10</sub> particles, where sea salt dominates the composition? can you still be sure for the last 2 sentences? Provide some explanation and arguments for this conclusion (L24-25).

Table 2. Provide median values as well, as the std is larger than the average...

Table 3. This table is not clear, which numbers represent number of samples and which mass concentration? What is the first line of numbers?

p. 3929, L1-2, have you checked the air mass back trajectories for these events, if yes, mention in the text.

p.3929, L5, there is no Fig. 4a, either correct the text or figure.

p. 3930, L8-9, also affected by the surf zone?

p.3931, L14-29. This discussion is confusing: high concentrations were attributed to marine source (L15-16), then the lowest concentrations were assumed to be biogenic (L27-28), but which lowest-during winter or summer (L26-27)? Details on how the percentages were evaluated should be presented.

p.3933, L7: fig.4?

p.3933, L7-9: defined how? From air masses? please specify how you attribute the OM to biogenic sources and then evaluate the possible contribution. L10:low volatility or solubility? Maybe layer not column?

p. 3933, L20: can you specify in what form the ammonium existed here? It should be in the form of ammonium nitrate or ammonium sulphate, as it can not be in the ion form. I understand the different sources for gaseous precursors, but the resulting ammonium would still be in either of these forms. One can discuss a different degree of sulphate or nitrate neutralization by ammonium, which would depend on availability of ammonia and thus biogenic source, but not to separate the ammonium from sulphate or nitrate, unless, you provide other possible compounds (ammonium chloride?, I doubt... sulphate would have a priority as sulphuric acid is the strongest among these acids...).

p.3937, L13-p.3938 L5: I tend to disagree, additional **biogenic** production would distort your correlation or produce an intercept, but won't affect the slope... however, in this case, the correlation is even better for the summer cases, discussion should be revised. I agree that additional photochemical production from anthropogenic sources could influence the slope, but these should be clearly separated. L16-17, I don't understand how the lack of surfaces to adsorb would increase the concentration? Adsorbed sulphate would also be measured as sulphate, so the resulting concentration should not change? It could change the form in which sulphate exists, but not the absolute value? Discussion should be revised. As well as the discussion in p.3931, L14-15, since there the whole increase in sulphate is attributed to biogenic sources.

p. 3938, L20-21, what do you mean by similar marine precursors- algae or compounds emitted by algae, if the latter, then sentence really need more arguments and proof.

p. 3938, L25, I don't see such a good correlation, some relationship, maybe. Provide either the scatter graph or correlation values or correct discussion accordingly. L 26, coincided, maybe, not correlated?

p. 3941, L3: What do you mean by the shorter residence time? Do you consider the difference in mixing time between 4 and 32 m considerable to have any effect? To my opinion, the difference appears due to different contributions from local particles and the ones originated further from the sampling location. It is obvious that lower sampling height would have larger contribution from local (fresh) sea spray particles.

p.3941, L 15: particles internally mixed with sea salt particles? What do you mean by that? Maybe, compounds internally mixed with sea salt in the same particles? Secondary production/deposition of gases on existing surfaces?

p. 3941, L25 and many other places, I would replace the sulphate and nitrate with sulphuric and nitric acid as those are acidic components, not the sulphate or nitrate. The same with oxalate and carbonate, those are salts...

p.3943, L2: Should also account for sulphate neutralization with ammonium as only the sulphuric acid that is excessive would participate in the replacement reaction...L6 and L21-23 what photochemistry reaction could be in place, please specify?

p.3944, L1-2. And where is the biogenic/marine factor of secondary sulphate discussed before? Secondary particles won't be internally mixed with the existing sea salt particles, therefore, should appear as separate factor, only sea salt particles serving as a sink for gaseous species would result in internal mixture and the same factor. Previous discussions on SOA production should be revised or PMF limitations discussed.

p.3946, L1-2, how pure were marine air masses, what were the criteria? Provide EC/nitrate concentrations for the "pure" marine air masses, does this imply depletion by biogenic sulphuric acid or anthropogenic emissions still had an influence?

Figure 1. Please specify the time interval and length for the trajectories presented, as well as specify that it is an ensemble. I guess c and d captions are switched?

Figure 2. Specify that it is PM<sub>10</sub>, correct the position of the ion sign (superscript + and -), correct ion nomenclature as well (NO<sub>3</sub> not NO3) and so on.

Cavalli, F., M. Viana, K. E. Yttri, J. Genberg, and J. P. Putaud (2010), Toward a standardised thermal-optical protocol for measuring atmospheric organic and elemental carbon: the EUSAAR protocol, *Atmos. Meas. Tech.*, 3(1), 79-89, doi:10.5194/amt-3-79-2010.