

## ***Interactive comment on “Long-term chemical characterization of tropical and marine aerosols at the CVAO: field studies (2007 to 2011)” by K. W. Fomba et al.***

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Author's answer to referee 2 comments: At first the authors wish to thank the referee for the critical reading and the helpful comments. In the following we will answer the comments and questions in detail:

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. Chlo-

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rine/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.

The requested consistency in the discussion is only an apparent problem and we have, therefore, for the sake of clarity rewritten some sentences and elaborated on our discussions for a better understanding. NSS-sulphate has definitely different sources. On the one hand it has natural processes (DMS oxidation) as source and on the other hand long range transported sulfate from the continents to the CVAO. It could be a primary emission of anhydrite or gypsum in parts of the Sahara (combined with elevated Ca levels) or it could be emitted as SO<sub>2</sub> from anthropogenic activities such as from power plants, traffic, etc., (combined with NO<sub>x</sub>) which could subsequently be oxidized during transport to sulfate. Thus, the attribution of secondary sulfate to either biogenic or anthropogenic sources is not contradictory but consistent with the air mass history of the type of sample investigated. With respect to chlorine/bromide depletion, we are aware of the neutralization of the acidic species by ammonium and have also elaborated on our discussion to clarify this aspect on pages 3943 L5-7. We have considered as first approximation total acid to show that other processes other than acid displacement reactions should be responsible for the chloride loss in this area. Including further neutralization processes will reduce the available excess acid and would only further justify the conclusion we already made. The chloride depletion in freshly emitted sea spray particles is low since these particles mostly have short atmospheric life times and thus less reaction time in the atmosphere for such processes to occur prior to their collection. Although PMF clearly identified this factor, we have not extracted the freshly emitted sea salt particles and aged sea salt particles from our filter data to perform chloride depletion on each of them. This could be considered in further works. Nevertheless, the freshly emitted particles will have very low chloride loss.

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Organic matter: In all samples, where OM and EC were elevated, anthropogenically released aerosols were the major sources. In cases of higher OM but low EC, biogenic sources were most probably the source of OM. As stated before this source differences have only been identified with respect to the air mass history in the samples investigated. 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?

In this work the PMF analysis was done on mostly soluble ionic aerosol components in addition to OC and EC. The obtained PMF solutions were interpreted on the basis of the air mass back trajectories, the meteorological and chemical composition of the filters. We excluded a one or two factor(s) solution since we were aware that in this region more than two factors contributed to the aerosol emissions while a four and five factors solution could not with less ambiguity be allocated to specific sources.

The factor selection criterion and statistical information on the factor solutions used and conclusions made in choosing these factors have been included as supplementary material. In the manuscript an indication to this supplementary information has been done on p.3924, L19.

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 sulfuric 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?

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"Pure" marine air masses do not mean "clean" in a sense of "non-contaminated or exclusively sea salt particles". The term "pure" was only used to identify air masses which had no contact with the continents within the last 5 days before reaching the CVAO. To avoid confusion, the term "pure" in the manuscript has been removed and as the case may be the sentences now read marine air mass. These air masses had low content of anthropogenic emitted compounds such as elemental carbon (EC). In other air mass categories, the EC content increases by a factor of about 7 during continental and Saharan air mass inflow and a factor of about 2 during European air mass inflow. According to table 5, the EC/NO<sub>3</sub><sup>-</sup> ratio increased by a factor of two during dust events and continental air mass inflow.

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].

The temperature of 105 °C was an error and the correct value is 110 °C. In our previous publication about the CVAO by Carpenter et al. (2010) we have published the correct pre-heating temperature 110 °C. The reviewers doubt about this temperature is reasonably. However, we buy pre-heated filters from the manufacturer. In our institute, the filters are further heated to 110 °C to desorb VOC. Our unpublished results showed that the blank values for OC and EC of the filters heated at 110°C were in the same range as those from filters heated at much higher temperatures. However, the mechanical stability (abrasion and breaking resistance) of the filters was better for the filters heated at 110 °C. Therefore, we have chosen this temperature for filter pre-treatments. Corresponding sentences have been included on p.3922 L 24-26.

p.3925, L3-17: reference to fig. 1 would help. The reference was introduced. p.3926, L24-28: can you provide some error estimates associated with the water error, e.g. in dust quantification. Clegg's model is a thermodynamic equilibrium model valid for 25 °C and appropriate for our sampling conditions. The estimated error of the water content was lower than 10 % or 0.5 µg/m<sup>3</sup>. The estimated error had negligible effect

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on the estimated dust concentrations since the value was far small compared to the uncertainty related to the determination of the other measured ions. A corresponding sentence has been included on L26-28 p.3926 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 PM10 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).

The definition of nss-sulfate has been added to the manuscript on P.3923 L 22-25. As the reviewer rightly comments, in marine particles the uncertainty is high. Thus, the last two sentences L24-25 have now been modified to now read, "During non-dust period long range transport from the northwestern African coast, Europe and other secondarily formed PM of oceanic origin were the main sources of nss-aerosol constituents."

Table 2. Provide median values as well, as the std is larger than the average... Median values have been inserted into Table 2.

Table3. This table is not clear, which numbers represent number of samples and which mass concentration? What is the first line of numbers?

Table 3 has been modified with the total number of samples (previously first line) now appearing below and the concentration ranges clearly stated on the first column.

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

This observation was made after studying the back trajectories and a corresponding supporting sentence has been added to the manuscript text on p. 3929 L2. p.3929, L5, there is no Fig. 4a, either correct the text or figure. The correction was made in the text. p. 3930, L8-9, also affected by the surf zone? "Mainly affected by the surf zone" was added. 3931, L14-29. This discussion is confusing: high concentrations were

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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.

Apparently these sentences were not clear enough and have been revised. L15-16: The high concentration is likely a combination of effects and not solely of marine sources as previously written. The increase in photochemical production and the increased emission of marine emission during summer could account for this increase. A corresponding sentence has been included in the manuscript text. The biogenic contribution was only estimated as the minimum possible contributing source since during winter biogenic activities are low and the minimum concentration was about 0.2  $\mu\text{g}/\text{m}^3$  and during summer the lowest observed concentration was 0.7  $\mu\text{g}/\text{m}^3$ . As a first approximation we have considered these minimum concentrations to be of biogenic origin. Using this assumption and comparing this minimum values to the total observed nss-sulfate concentrations during these seasons; we have estimated the minimum possible biogenic contribution. However, this contribution could for particular cases be higher such as during periods of higher DMS emissions in summer.

Corresponding sentence has been included on L14-16 p-3931. p.3933, L7: fig.4? Figure 3 was wrong – it has now been corrected. 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?

It has been shown that the ocean surface microlayer is enriched in organic material and this material can be emitted to the atmosphere via bubble busting. We therefore assume that the ocean emitted organic matter, may be of biogenic sources. We can, however, not quantify the amount of organic matter since such experiments were not carried out during this time period, however, according to literature studies, it has been shown that organic matter from ocean can be emitted to the atmosphere and we have drawn our conclusion on this premise. An additional sentence has been added on

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p.3933 L-9. L10: The right words are low solubility and Layer. These have been changed. 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 cannot 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...).

We did not find a correlation between Ammonium and nitrate and therefore the presumption that they may have different major sources. Ammonium nitrate is not stable in such tropical region such as at the CVAO due to high temperatures ( $>25^{\circ}\text{C}$ ). We, however, think that ammonium is most likely present as ammonium sulfate as also suggested by the reviewer. We have found from size resolved measurements that ammonium is mostly found in the submicron particles while sulfate is observed in both submicron and supermicron particles. From the PM10 data set discussed here, it is not trivial to easily find out in which size fraction these compound exist. Free  $\text{HNO}_3$  reacts predominantly with  $\text{NaCl}$  whilst ammonium produces a stable compound after reaction with sulfuric acid which could be available from the oxidation of DMS. However, the presence of ammonium at the CVAO is not necessarily linked with sulfate from anthropogenic sources. We have, however weakened our conclusion and sentence now reads, "These ions might have had other sources".

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 under-

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stand 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.

The discussion has been revised on both pages P.3931 L14-15 and P 3937, L13-P.3938 L5. During summer the photochemical production of the particle phase nitrate and sulfate is higher and the production of nss-sulfate from marine precursors such as DMS may also increase. This may therefore lead to the observed increase in the nss-sulfate concentration reflected by the increase in the slope. The combined effects of increased winter emissions of anthropogenic precursors and the reduced winter and enhanced summer photochemical conversion and summer enhanced ocean emissions might explain the effect depicted in Figure 5. However, further investigations are necessary in order to clearly explain the depicted difference.

Corresponding sentences have been added on P 3937, L13-P.3938 L5 and P.3931 L14-15.

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.

This sentence was may be unclear and has now be revised to read as follows. Thus we conclude that both nss-sulfate and oxalate could have originated from different precursors of marine origin such as from marine organisms' e.g algae or from their emissions.

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?

You are right that our formulation is too optimistic. We have changed good correlation

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to coincidence and we have also weaken our conclusion on p.3939 L7-9 to become "The observed coincidence between ammonium and chlorophyll a may suggest that the ocean might be a source of ammonium in this region"

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.

At the lower sampling height, fresh sea spray particles from the surf zone dominate the collected particles. In these particles the deficit for bromide und chloride is low since these particles do not stay longer in the atmosphere before their collection. The surf zone has negligible effect on the particles collected at the 32 m height and since we cannot differentiate freshly emitted particles that finally reach the tower height during windy conditions and those that are long range transported, we consider those sea salt particles that reach the tower to be mostly different in terms of their residence time from those at the 4 m height dominated by the surf zone influence. Earlier already described by Niedermeier et al. (2014) the surf zone does not affect the PM collected at the tower thus sea salt particles arriving at the tower have longer atmospheric residence time than those at the 4m height. We have however revised the sentence for a better understanding on P.3941 L3. 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?

Particles with longer atmospheric residence time may react with gaseous compounds, e.g. sulfuric and nitric acid. In clouds the processing between particles and gases can result in mixtures of sea salt and anthropogenically released particles or gaseous precursors - so internally mixture particles can be formed. However, the word "internally" has been removed from the sentence to avoid any misunderstanding. p. 3941, L25

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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...

These aspects have been changed and the new formulation is reflecting this fully accepted criticism at other places, too.

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?

The discussion of neutralization with other cations such as ammonium has been included on lines L5-L7 p.3943. Possible heterogeneous photochemical reactions such as those of NaCl with ozone or NO could apply (W. Behnke & C. Zetsch Journal of Aerosol Science 21 1990, 229-232). A corresponding sentence has been added to the manuscript.

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.

It is true that the freshly emitted nss-sulfate e.g from marine sources may not have enough time to get internally mixed with freshly emitted sea salt particles, but subsequently depending on the residence time of the sea salt particle these gaseous species may condense on the existing sea salt particles, thus, the term aged sea salt particles. Secondarily produced sulfate can also be externally or internally mixed with sea salt particles depending on the residence time of sea salt particles. Therefore, all three factors do contain a degree of sulfate. The sea salt sulfate is found together with the sea salt factor. The fresh sea salt factor only represents the sea salt sulfate fraction only. The long range transported sulfate is also found in the long range transport factor.

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The aged sea salt particles also have some sulfate since they may also have sulfate coatings depending on how long the particle stays in the atmosphere. The discussion on SOA production and PMF limitations has been revised accordingly in the previous comments above.

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?

The answer to the discussion about pure and clean has been provided above. The Table 5 shows the differences for the major aerosol constituents found in aerosol samples influenced by their origin and time over the ocean. A really "clean" air doesn't exist in this region but the influence of anthropogenic contributions differs between the groups of Table 5. The word pure was used only to differentiate marine air mass from the other categories and only imply air masses that had spent more than 96 hrs over the ocean. For the sake of clarity the word pure has been removed.

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?

Changes were made on the caption. All trajectory ensembles in this figure represent 96 hours back trajectories calculated hourly over the collection time of the samples. The error from the switched figure captions C and D has been corrected.

Figure 2. Specify that it is PM10, correct the position of the ion sign (superscript + and -), correct ion nomenclature as well (NO<sub>3</sub> not NO<sub>3</sub>) and so on.

The corrections have been made.

Please also note the supplement to this comment:

<http://www.atmos-chem-phys-discuss.net/14/C2962/2014/acpd-14-C2962-2014-supplement.pdf>

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