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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Assessing the role of anthropogenic and biogenic sources on PM_1 over Southern West Africa using aircraft measurements" *by* Joel Brito et al.

Anonymous Referee #2

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The manuscript presented data from the DACCIWA project over south west Africa. With PMF analysis of AMS OA data, three factors were resolved: fresh and aged urban OA and a generic OOA. Using tracer methods, the contribution of IEPOX-OA and pON and the effects of anthropogenic and biogenic sources were discussed. It was found that IEPOX-OA is a major fraction of OA, contributing 24% and 29% for background and in-plume conditions, respectively.

There are very few datasets from Africa and the data presented here are interesting and will be of interest to the scientific community. The manuscript is generally well-written. However, I have some concerns regarding the data analysis, specifically on

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the estimation of IEPOX-OA and pON concentrations.

It is difficult to understand the IEPOX-OA apportionment data. The authors noted various intrinsic reasons regarding why this factor might be challenging to resolve from PMF analysis for airborne data. However, these limitations apply to most (if not all) airborne data but other previous studies were able to resolve an IEPOX factor from flight measurements (e.g., Hu et al., ACP 2015 and references therein; Xu et al., JGR 2016). Are there something else causing a difficulty in retrieving this factor? Have the authors tested different FPEAKS in their PMF analysis, or use ME-2, or, have the authors preformed PMF analysis only on the subset of data where there might be a larger amount of IEPOX-OA (e.g., near the Abidjan area)? More analyses are needed to demonstrate and justify the results.

It is not clear why an IEPOX-OA factor cannot be resolved from PMF analysis, yet the tracer method suggests that ~30% (i.e., a large fraction) of the total OA is IEPOX-OA. Firstly, in PMF analysis, both variations in mass spectra and time series are taken into account. Even if the time series of IEPOX-OA are similar to other factors, the mass spectra of IEPOX-OA is very unique and has a distinctively high intensity peak at C5H6O+ (m/z 82), and this is what allows it to be resolved from other generic OOA factors in the first place. Secondly, it is possible that PMF analysis cannot resolve a factor if the contribution of that factor is too small. However, based on the tracer method, IEPOX-OA is a major fraction of ambient OA (~30%). One concern is, can be concentration of IEPOX-OA be drastically overestimated in the tracer method due to the use of f82 instead of fC5H6O+ (as discussed in Hu et al., ACP 2015), given the interferences from urban and biomass burning emissions, which are also prevalent in the region? The authors should look into this further, and provide explanations and justifications regarding these drastically different results (PMF vs. tracer method).

Regarding pON analysis, it is not clear form the manuscript, but it appears that 46/30 ratios are used in the analysis instead of NO2/NO? (If not, please discard my comment below and simply clarify this in the manuscript). The approach to estimate pON re-

quires the use of NO2/NO (or NO/NO2). The are other organic ions at m/z 30 (CH2O). Therefore, using 46/30 ratio will lead to uncertainties in the pON estimation, and yet, such uncertainty cannot be quantified as there is no way to tell the relative importance of CH2O and NO at m/z 30 for ambient data (if the instrument m/z resolution is not high enough to resolve these two ions at the same m/z). If the instrument m/z resolution is not high enough, one cannot use the R method to estimate pON with confidence.

As a large portion of the discussions and conclusions in this manuscript hinged on the IEPOX-OA (and relatively less so on pON), more analyses are needed to demonstrate the robustness of the results and conclusions in this work. Overall, I think the manuscript can be published in ACP eventually, provided that the major concerns are addressed.

Specific comments.

1. Page 3, line 11. It is noted that previous work estimated biogenic SOA of remote forested areas over west Africa is on the order of 1 ug/m3. Can the results from the current study be put in the context of this previous work? Fig. 6 appears to suggest that IEPOX-OA is about 1 ug/m3?

2. Page 4, line 14. Should be “southeastern”. Also, would be appropriate to also cite Xu et al., 2015 ACP which focused on estimation of particulate organic nitrates in the southeastern US.

3. Page 14, line 17. Note that a recent review paper by Ng et al. 2017 ACP has a summary figure on “observations of pON concentrations over a wide range of locations”.

4. Page 5, line 2. What is the m/z resolution of the C-ToF-AMS used in this study? Please specify clearly. Is it high enough to differentiate between the different ions at the same m/z? This has important implications for the subsequent IEPOX-OA and pON analysis.

a. Page 6, line 16. What are used in the pON analysis, NO2+ and NO+, or 46 and 30?

In the formula, R is the ratio of NO2+/NO+. If the m/z resolution of the instrument is not high enough to differentiate ions at m/z 30 (NO+ vs. CH2O+), and 46/30 ratios are used in the calculations of pON instead of NO2+/NO+ ratios, this will lead to uncertainties in the estimated pON mass concentrations. Further, as the contribution of NO+ ion to m/z 30 is unknown, one cannot tell how large the uncertainties are in the estimated pON mass concentrations. With this, if the m/z resolution of the C-ToF-AMS is not high enough, I do not think that one can use equations 1 and 2 to evaluate pON mass concentrations with confidence. Conversely, if the m/z resolution of the instrument is high enough, please simply discard the above comment specify clearly.

b. Page 6, line 23. For IEPOX-OA, the use of m/z 82 as a tracer will have a higher uncertainty than using the C56O+ ion, and can be particular sensitive to the f82 background value, which can vary widely in the presence of urban and biomass burning emissions (Hu et al., ACP 2015). The authors shall at briefly discuss the uncertainties associated with the use of f82 instead of fC5H6O+ here.

5. Page 6, line 17. Note that the RorgNO3 value = 0.1 is an assumption. This number can depend on the type of organic nitrates measured (isoprene, monoterpenes, etc) and instruments (Xu et al., ACP 2015; Kiendler-Scharr et al., GRL 2016). That the value is assumed (and not known for sure) to be 0.1 needs to be made clear in the manuscript.

6. Page 7, line 25 onwards. The authors must include some details in the SI to justify the choice of the PMF solution. How and why is a 3-factor solution chosen? Please discuss Q/Qexp, effects of seed, FPEAK, correlations of time series with external traces, correlations with reference mass spectra, etc. It is important that when one presents PMF results in a manuscript, one shall also present the details on how the specific PMF solution is chosen and clearly justify the choice of the solution.

7. Page 8, line 16 to line 25. It is noted that PMF cannot resolve an IEPOX-OA factor and the biomass burning factor. (see main comment at the beginning of review)

a. Have the authors tried different FPEAK values? Or, have the authors tried using ME-2 and constrain the IEPOX-OA? Please discuss.

b. In line 26 onwards, the authors focused on IEPOX-OA in the Abidjan plume. Here, the authors noted that the IEPOX-OA accounts for 60% of total OA mass with increased plume age (line 22, page 9). With this, it is very puzzling that the tracer method results in such dominant contributions from IEPOX-OA to total OA, yet the PMF analysis cannot resolve this factor. Have the authors performed PMF analysis only on the data taken around Abidjan (Fig. 1). If IEPOX-OA indeed contributes such a large fraction of total OA near Abidjan, (and IEPOX OA has a very unique signature in AMS), I would imagine one can resolve this factor from PMF analysis of data taken around Abidjan.

8. Page 9, lines 1 and 7. CO, NH4 and BC data are discussed but not shown. Please also show the data in the figure (or in the SI if the authors deem the figure to be too busy).

9. Page 9, line 1. It is noted that NO3 concentration is also significantly lower in the advecting air mass than continental background. However, this does not seem to be case based on the data shown in Fig. 5. They are both low.

10. Page 9, line 29. It is noted that the enhancement ratio of IEPOX-OA tends to increase with plume age, indicating a net production of organic matter through this pathway. What is the mechanism for the net production with increased plume age?

11. Page 10, section 3.3. The results presented in this section are very different from the Abidjan plume.

a. Can one then assume that the large contribution of IEPOX-OA in the Abidjan plume is a special case, but not a representative of the plumes in the region? Please discuss and clarify.

b. Page 11 line 10. It is noted that IEPOX-OA and pON concentrations are also enhanced in the urban plumes. However, this statement is not consistent with the data

from Fig. 6, which seem to show that the IEPOX-OA and pON concentrations in the plume vs. background are very similar.

c. Page 11 line 10 onwards. Back on page 9 line 8, the authors noted that the changes in IEPOX-OA concentration in the advecting mass vs continental background for the Abidjan plume (i.e., no IEPOX-OA in the advecting mass) suggests that IEPOX-OA is formed locally. But in Figure 6, the concentration of IEPOX-OA in the regional background is the same as in plume, does this mean that IEPOX-OA is not formed locally?

d. Further, if I am understanding correctly, now the tracer method (f82) is applied to ALL in-plume and background data to determine IEPOX-OA concentration? Again, if the contribution is so high (page 12 line 10) at 25-30% of OA in general, it is very difficult to understand why PMF analysis did not resolve the IEPOX-OA factor.

e. Page 11, line 25. Missing de Sa et al. ACP (2017) in the reference list at the end of the manuscript.

f. Page 11, line 29. It is noted that "Although we show in the previous section a significant enhancement of IEPOX-OA within urban plumes (particularly during the Abidjan flight described in Section 3.1)". Again, data in Fig. 6 do not show a significant enhancement of IEPOX-OA in the urban plumes, and that it appears that Abidjan flight is a special case where IEPOX-OA is largely enhanced in that plume (but not for other plumes).

12. Page 12, line 3-14, discussion of Figure 7.

a. The data shown in Fig. 7 are very scattered. Nevertheless, one thing to notice is that it appears that the slope of IEPOX-OA vs. SO4 is the most similar to ground data in the SE US (Xu et al., PNAS 2015), but also falls somewhere between those observed for flight data in the SE US (Xu et al., JGR, 2016) and ground data from Amazon (de Sa et al., ACP 2017).

b. I do not understand the discussion regarding NOx. Firstly, can the authors color

the data points by NOx, similar to de Sa et al. (ACP 2017) and see if there is a trend? Secondly, it is not clear why the change in the fraction of IEPOX-OA will be interpreted as a change in the driving mechanism in IEPOX-OA formation. Based on the IEPOX-OA concentration (not fraction) vs. SO4 data, it appears that SO4 plays a role as shown in the previous studies. It is not clear why the fraction will provide specific insights regarding the formation mechanism. Please discuss and elaborate.

Technical comment. 1. Page 12, line 1, "x" in NOx should be a subscript.

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