Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2019-838-RC1, 2019
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Atmospheric Chemistry and Physics Discussions

# *Interactive comment on* "Insights on Atmospheric Oxidation Processes by Performing Factor Analyses on Sub-ranges of Mass Spectra" *by* Yanjun Zhang et al.

**Anonymous Referee #1**

Received and published: 27 December 2019

This manuscript promotes two new approaches to analyze complex mass spectra (here of highly oxygenated molecules (HOM)) with the goal to extract as much as possible information from the whole mass spectroscopic information: binwise PMF and coordinated PMF analysis in selected mass ranges. The authors suggest to select certain mass ranges for analysis according to expected time scales of production processes and sink processes, whereby they have condensation loss as major sink in mind. The approach is exercised at an ambient data set, measured by NO3-CI_API-TOF in September 2016 at the SMEAR II station in Finland. The manuscript is very well written, it is informative and very interesting to read. It discusses the limits (and strengths) of PMF analysis of atmospheric observations in the context of the variabil-



ity of production and sinks processes of gaseous compounds in the atmosphere. It also points out two new observations - day time dimers and night time dimer nitrates-, which need mechanistic explanations. The focus of the paper is on the methodology, although along its development it reveals insight into HOM formation processes. I suggest highlighting the latter already more in the Discussion sections and summarizing it again in Atmospheric Insights section. I also suggest shortening the Contaminant Factor section and place some text from here into the supplement. See also comments. In the larger parts I see the manuscript - even in its given form - as an original and important contribution of general interest to atmospheric scientists, as nowadays in many atmospheric fields research is based on high resolution mass spectrometry. I suggest publishing the manuscript in ACP after the authors have addressed the (minor) comments below.

Comments

Abstract, line 36: Don't present your new findings as appendix. "As two mayor insights of our analysis scheme, we identified daytime dimer formation. . . We separated dimer formation by NO3 oxidation. . .. "

Introduction, line 87: Could the authors comment on the role of chemical losses compared to condensation losses onto particles. Couldn't chemical losses, e.g. by oxidation of HOM by OH, enhance the window of sink time scales?

Introduction, line 93: Peräkylä et al., 2019 is not a suited reference for such a general statement.

Introduction, line 121: The impact of the oxidants is different at different times of the day. That should limit important formation pathways to less than 6.

Introduction, line 126: RO2 + RO2 also lead to monomer termination products. Thus, the statement is not valid in such generality. Maybe on should modify the sentence: . . ..in monomer products (not terminated by RO2), dependent on only one oxidant. . ..

Introduction, line 145: It would be wishful to refer also already here to the new atmospheric information not only to “meaningful factors”. In the sense of “we will show that we were able to separate process x from process y”.

Result, line 295: This sentence is hard to understand, please, split and reformulate.

Discussion, line 448: hard to understand and possibly a verb missing. Please, reformulate.

Discussion, line 468 and 474: Did you search for specific marker ions (odd mass) in the monomer range? Maybe, singular nitrates are formed quite efficiently and the corresponding nitrate peroxy radicals could be involved in the dimer formation. Could NO3 radicals attack the dimers the dimer?

Discussion, line 485-548: I find that whole section too lengthy. I agree that the authors performed a smart analysis to find out why contamination factors do correlate or not. However, is this argumentation really needed to demonstrate that different loss rates lead to different time profiles, thus attribution to different factors, if the source is the same?

Insofar I find the jump from the contamination analysis to ambient data in line 541 somewhat disturbing. At least a new paragraph should start here.

I suggest to place the text of contamination analysis in large parts into the supplement. In the manuscript I would just state that a detailed analysis explained why contamination factors do not correlate and refer to the supplement. The space saved could be used to more underline the atmospheric findings somewhat more (all over the manuscript and in the Atmospheric Insights section).

Atmospheric Insights, line 550: “While the previous section discussed several findings with atmospheric implications,..” I suggest to sample and to discuss at this point the insights into the HOM formation processes mentioned in all the discussion sections. And maybe elaborate the two new findings somewhat more.



Conclusion, line 633: As mentioned before, highlight the new atmospheric findings here. Prevent presenting it as an appendix to your methodological approach.

Minor

Figure captions are not separated well from running text.

line 119: any instead of many ?

line 468: Please, replace “this factor” by the name of the factor “factor R2F4_N” for faster readability, because there was more than one factor listed in the previous sentence.

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