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Interactive comment on "Source characterization of Highly Oxidized Multifunctional Compounds in a Boreal Forest Environment using Positive Matrix Factorization" *by* Chao Yan et al.

Anonymous Referee #1

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The authors analyse field observations of highly oxidized multifunctional molecules (HOM) by nitrate CIMS in Boreal forest (Hyytiälä). A period of more than 4 weeks was used to investigate in how far PMF would help to understand the (chemical) origin of different groups of HOMs. Critical points in PMF are the selection of the number of factors and appropriate treatment of errors. The authors find that three PMF factors are sufficient to catch major source signatures, however, 6 factors are more suited to describe evident finer details. The six factor solution is formally acceptable within the mathematical PMF control framework. The authors underline that formal criteria are not sufficient to judge PMF solutions and discuss the factor profile (MS) and factor time series in context of laboratory MS and the time series of other field observations.

The authors spent substantial efforts in determining the error matrix, which they try to describe in the supplement. The main manuscript is well structures and well written; figures and table were well selected. The manuscript is interesting to read. Unfortunately, the supplement is much weaker than the manuscript itself and suffers from typos and "looseness". By these and somewhat unclear notations it is difficult to follow it in large parts. This is unfortunate because a better edited supplement clearly could strengthen the whole manuscript. The value of PMF, especially in MS containing mainly molecular information (no fragmentation) is under debate. I think the results of this paper show that PMF applied in suited way to HR-CIMS can indeed help interpretation of field data. The manuscript should be published in ACP after a fes minor revisions. However, I urgently suggest to the authors to revisit their supplement and provide a better and clearer edition.

A general remark: I think the manuscript is very good and interesting. However, in parts you are using a relatively formal language. This is ok if you talk about general PMF. However, you are analyzing mass spectra. For a general reader (and me) it would be helpful if you would breakdown the general mathematical notations to the items you are de-facto dealing with: variables -> peak positions or m/z, analytical uncertainty -> standard deviation of instrumental noise, DL/3 -> 1sigma detection limit, DL -> 3sigma detection limit. etc. (see also below remarks to supplement).

Minor comments:

line 114: I think, only (X-H)- should appear in the numerator of eq. 1, as (HNO3)*(X-H)- is redundant and has the same mass as (NO3)*X-, and so on for i>0

line 167f: Let us assume overlap of two compounds, nearly the same mass and similar intensity arising in two different factors. How would you deal with separation of the right compound into the right factor? Isn't the argument, that you do not have much of such overlap? Therefore you can use UMR and determine the according elemental composition later. Did you apply any diagnostics to show that overlapping peaks of minor importance?

line 179: How would you define contributions to analytical uncertainty? Is it instrumental noise, is it background, is it interferences at or near a given m/z? I think the manuscript and even more the supplement would become clearer if with a more consistent and traditional notation.

line 199: Where does the value DL = 0.105 come from? I guess it is no accidence that it is 3 x “the background for all tunings in the ‘blank mass’ (800∼1000 Th)” “estimated to be 0.035”. I think this is confusing, see previous remark..

line 388ff: How does the dimer analysis of factor type -1 compares to factor type-2 in Figure 9 ? Do you find nitrate containing dimers?

line 404ff: Could one state that daytime type 1 factors is of special (relative) importance when UVB and OH are low, thus daytime ozonlysis gains in importance?

line 413 and 434: Plants emit more than monoterpenes (even toluene): could isoprene, methyl salicylate, or so called leaf alcohols play a role?

line 433f: “could” maybe better than “may”

line 456: “in principle” maybe work better as “theoretically. No theory in involved, only expectations.

line 461 and Table 2: Are these uncentered correlation (UC) coefficients as announced in line 333 ? Please clarify.

line 477: You are revealing the chemical sources with exception of the transport factor. Is it possible to check for correlations with monoterpene emissions or so? Could that help for the non-C10 observations?

Figure 1 and Supplement Line 95 + 112f: Eq. S1 should be also plotted in Figure 1. Otherwise I cannot understand why there are lines for AMS and lab results, but a range for ambient data approach. More important, as I understood you expect to determine the upper limit of your error by analysis of the ambient data. This was inherent to the method applied, as you could not exclude real chemical variations within the analysis interval. Why is the lab approach almost at the top error boundary of the approach using ambient data. Isn't that a contradiction?

typo and errors line 101: Eastern line 254: Mix of singular and plural line 419: Tröstl et al is missing in the reference list

SUPPLEMENT

line 5: Why is ion detection by HR-CIMS more complicated the by AMS? I think it is easier because of limited fragmentation.

line 8: How does transmission affect signal background ? Because of real signals arising from "contaminations"?

line 9: No a-value in eq. 6!

line 12: Mix of singular and plural.

line 14: mlpm in manuscript

line 15: “without generating large turbulence” I doubt that looking at your set up in Figure 1. Moreover you want turburlence to mix your calibrant with the main flow.

line 16: This last sentence does not make really sense: “vacuum line”?

line 20: “used IN the permeation source”

line 26: Eq. 5 ?

line 26f: I understand background as “offset”. But you are looking at instrumental noise?! The background, I would determine around each m/z = 0.5UMR, i.e. between two peaks. I also would try to determine the instrument noise there.

line 31 and Fig. S3: I think, there is a trend of increasing “back ground” with decreasing m/z. 0.035 is background or instrumental noise, or detection limit ? See my previous

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Discussion paper

comment.

line 35: eq 6 ??

line 51+ 54: “median over a short period of time (5 data points)”; does that mean over 25 min.? Then you might have indeed to consider influence by chemical changes!?

line 55f: I really don’t understand what you did. Especially the last half sentence is unclear. Try to reformulate in clearer way.

line 64f: “dividing the “noise estimate” (i.e. signal minus trend) data into bins”; difficult to understand.

line 69: S1-S9 (?), but you need 10 bins! From here on, you mix the notation “S1- S9” and the fact that your using 10 bins. Check text and figures for that and correct.

line 73: 940? or 9084/10??

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