Comments from referees are in black, and our responses are in green.

Response to the comments of referee 1:

General Comments

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 few 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).

We would like to thank the referee for the helpful and detailed comments and suggestions.

According to the comments, we modified the manuscript in the following aspects:

1) Improve the supplement to make it more clear and easy to follow;
2) Replace the formal PMF language by mass spectrometry-oriented terminology to make the manuscript easily followed by general readers, such as Eq.2, Eq.6, and corresponding notations in the supplement.

In the following, we reply to the referee's comments item by item.

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

This equation is the same as used by Ehn et al. (2014). We used this equation here to emphasize our awareness of structurally different clusters with the same elemental composition, such as $(HNO_3)(X\text{-}H)^-$ and $X(NO_3^-)$. In practice, we are unable to distinguish them. We will simplify this equation as below:

$$[HOM] = \frac{HOM(NO_3^-)}{\sum_{i=0}^{2}(HNO_3)_i(NO_3^-)} \times C$$

We also omit the cases of $HOM(HNO_3)NO_3^-$ and $HOM(HNO_3)_2NO_3^-$, as in our analysis, these clusters' contribution are minor.

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?

In principle, PMF should be able to correctly attribute that (unit m/z) signal to two factors, with ratio equal to their actual contribution to the total signal at that m/z. The same issue can occur also in HR data, if a certain molecule has two different sources, then properly configured PMF will separate the signal from that molecule into two different factors. This is, in fact, one of the strengths of PMF.

Peak overlap on one unit-mass was indeed observed in our spectrum, but we did not perform any diagnostics analysis to show the potential effect of peak overlap, since we think this method should not lead to large uncertainties in our case for following reasons:

1) when interpreting factors, we often rely on fingerprint molecules and the most evident difference between factors is whether their fingerprint peaks contain nitrogen atoms, which are easy to separate simply from their masses (odd or even masses according to the "nitrogen rule", assuming closed shell products).

2) the most prominent peaks in our spectra are almost always dominated by one peak (usually > 90 %). In such cases, ignoring the minor peaks, which are more likely to be assigned correctly, probably would not lead to large uncertainties. When we determine fingerprint molecules for each factors, we only choose single or overwhelming peaks (e.g. Table 1 and Fig. S9).

3) in some cases, overlapped peaks are very likely from the same formation pathway so that we don't need to consider their separation by PMF. One example is that $C_{20}H_{32}O_{10}$ and $C_{19}H_{28}O_{11}$ overlap on mass 494 amu, but they are both dimer compounds likely from RO_2-RO_2 reaction, and indeed, PMF attributes the entire signal at 494 amu into the same factor.

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.

The analytical uncertainty (σ_{ij}) is from counting statistics. As the number of available molecules is high, but the probability of ionizing and detecting such molecules is low, we can assume that the probable distribution of detected ion numbers for a given molecule population can be modeled as a Poisson distribution (Allan et al. 2003).

Allan, J. D., Jimenez, J. L., Williams, P. I., Alfarra, M. R., Bower, K. N., Jayne, J. T., Coe, H., and Worsnop, D. R.: Quantitative sampling using an Aerodyne aerosol mass spectrometer 1. Techniques of data interpretation and error analysis, J. Geophys. Res., C: Oceans Atmos., 108, 2003.

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.

We had some confusing terminology in the supplement. The background determined from "blank mass" is the standard deviation (1σ), and we define DL as 3σ, that is why DL=3*0.035. We will change the terminology in both the main text and the supplement. Such as in Eq.6, the DL/3 is replaced by σ_{noise}, which is more straightforward.

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?

Yes, we have also checked the dimer distribution of nighttime type-1 factor, as shown in Figure 1. Though we see some mononitrate dimers in this factor, their contribution is small (16 %) compared with non-nitrate dimer compounds (84 %); the dinitrate dimers are not present in this factor. We think this is reasonable: these mononitrate dimers most likely have one parent RO_2 from O_3 + monoterpene reaction, so their temporal variation should also be affected by O_3 + monoterpene (type -1 factor); the parent RO_2's of dinitrate dimer are both from NO_3 + monoterpene, which has no dependence on O_3 + monoterpene, so they are not present in type -1 factor. We will mention this in the main text.

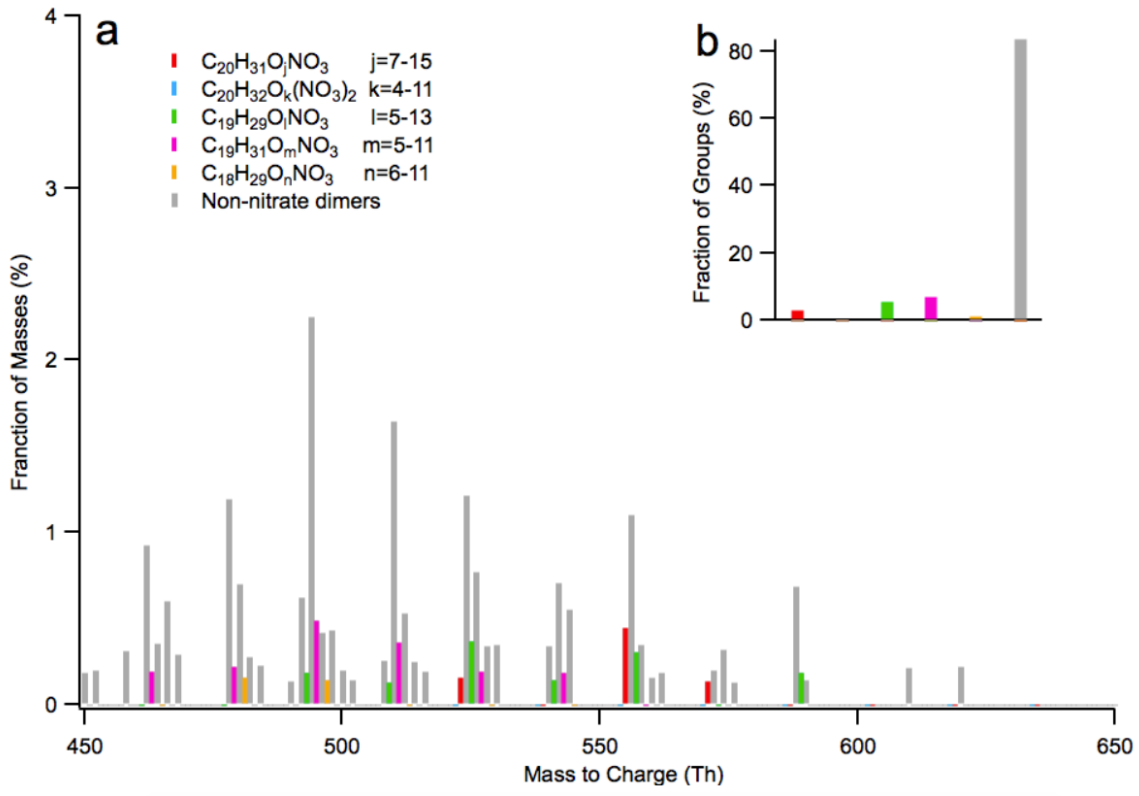

Fig. 1. Dimer profile of the nighttime type-1 factor. All dimer peaks are assigned to six groups based on their elemental formula and marked with different colors. Fig. 1a shows the location and mass fraction of individual peaks, and Fig. 1b gives the fraction of these groups.

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?

The reviewer is correct that, in general, daytime ozonolysis will be the dominant loss pathway for monoterpenes during overcast days, as the OH levels stay low compared to sunny days. However, as so many other important parameters are also affected to a larger or smaller extent (e.g. ozone production, temperature mixing height, monoterpene emissions) we prefer to not discuss the possible effects following meteorological changes further than stating the suggested main oxidants in Table 2 in the paper.

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

We cannot rule out the potential contribution of other compounds, but the predominance of molecules with ten C atoms in them for each factor, together with good agreement with reference monoterpene spectra for most factors, suggests that monoterpenes are the main contributor. For isoprene, its concentration is low at our measurement site as measured with PTR-CIMS, and its oxidation products, such as $C_5H_{10}O_x$, are only minor signals in our spectra.

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

Agreed, we will change it to “could”.

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

Agreed, we will change it to “in principle”.

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

These were not UC coefficient, but Pearson's linear correlation coefficient. We changed to UC coefficient. The two types of coefficients give a similar picture.

Table 2. Suggested HOM formation pathways represented by each factor, and the uncentered correlation coefficient between factors and other relevant conditions. In total, 1491 data points (30-min time resolution) are used. *These species cannot be ruled out.

Factors	Suggested main oxidant	Suggested main RO_2 terminator	correlation coefficient (R, n=1632)			
			NO	H_2SO_4	UVB	T
Nighttime type-1	O_3	RO_2	-0.05	0.19	0.14	0.26
Nighttime type-2	NO_3	RO_2	-0.07	0.18	0.06	0.33
Daytime type-1	O_3	NO (*HO_2)	**0.38**	0.56	0.50	0.42
Daytime type-2	OH (*O_3)	NO (*HO_2)	0.22	**0.76**	**0.84**	0.69
Daytime type-3	OH (*O_3)	NO (*HO_2)	0.29	0.56	0.66	**0.80**
Transport factor	-	-	0.41	0.48	0.44	0.51

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?

While some monoterpene emission measurements are available, these are not easily up scalable to regional scale that would be required here. But in any case, the actual monoterpene concentrations would be the more useful comparison. Unfortunately, the data quality of monoterpenes measured by PTRMS was not very good for this period. However, in general, the diurnal pattern of monoterpene shows low concentration in the daytime and elevated concentration during the night, driven by variations in mixing height. This trend is similar to our nighttime factors but opposite to all daytime factors, even though we are confident (e.g. based on chamber studies) that the main daytime HOM signals are from monoterpene oxidation.

In other words, while it is very possible that other VOCs than monoterpenes contribute to the HOM spectra, it is unfortunately not easy to draw any conclusions on this from the measured VOC concentrations we have available.

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.

Agreed. We now revised the equation for this ambient data approach, and plot it in Figure 1.

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?

The lab-derived estimate and the error estimated from ambient data are estimated from two independent statistical methods, as described in the text, and our primary aim was to see if the two estimates roughly match each other. The shown agreement in Figure 1 is quite good considering this inherent difference, and should not be considered in contradiction.

typo and errors line 101: Eastern line 254: Mix of singular and plural

We now corrected these typo and errors.

line 419: Tröstl et al is missing in the reference list

We added Tröstl et al (2016) to 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.

Our sentence was confusing. What we want to emphasize is that CI-APi-TOF is usually set to detect ions on a much broader mass range, over which the detection efficiency (transmission) might change significantly. We need to examine if the transmission affects the counting uncertainty. We will remove this sentence.

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

This was indeed improperly phrased. What we wanted to emphasize is that whether the transmission will influence the signal counting uncertainty is unknown and needs examination. We will modify it as "Its potential influence on signal counting statistics needs examination."

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

It should be eq.7 instead of eq.6. We will correct it.

line 12: Mix of singular and plural.

We rephrase the sentence as "A temperature controlled permeation source was connected to the CI-inlet"

line 14: mlpm in manuscript

This is a typo. It should be milliliter per minute (mlpm) in the supplement.

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.

This is the same typo as in line14, the unit “slpm” should be “mlpm”. We will correct this typo in the figure.

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

We rephrased the sentence in line 16 as “The outflow of the permeation source was further diluted by N_2 flow (~ 10 lpm) before entering the chemical ionization inlet (CI-inlet) as the sample flow. The flow rate of the sample flow could be adjusted by varying the total flow and/or sheath flow of the CI-inlet, which were set to 30 lpm and 20 lpm, respectively. All these flow rates were kept identical throughout the set of experiments.”

line 20: “used IN the permeation source”

Agreed, we now replaced “as” by “in”

line 26: Eq. 5 ?

“Eq.5” should be “Eq.6”, we now changed it.

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.

The “background” is misused, which should be the standard deviation of instrument noise. We replaced this by “σ_{noise}”. Getting instrument noise from masses between two peaks is a good suggestion and we now applied both methods on the ambient dataset, and the difference is shown in Fig. 2 below. At masses above 600 Th, there is little difference between the two methods. At masses below 500 Th, in the “0.5UMR” method, the σ_{noise} decreases, which might be caused by the counting algorithm when averaging the raw data, e.g. baseline removal.

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 C4 comment.

There is indeed weak increase (~ 0.005 cps / 200 m/z) of σ_{noise} (on both methods) with decreasing mass. We will rephrase the description of this figure. In this study, we took the median number (i.e. 0.035) over this mass range (800~1000). On the other hand, we consider this weak increase likely unimportant for the overall error estimate, because the analytical uncertainty (σ_{ij}) is overwhelming in most cases.

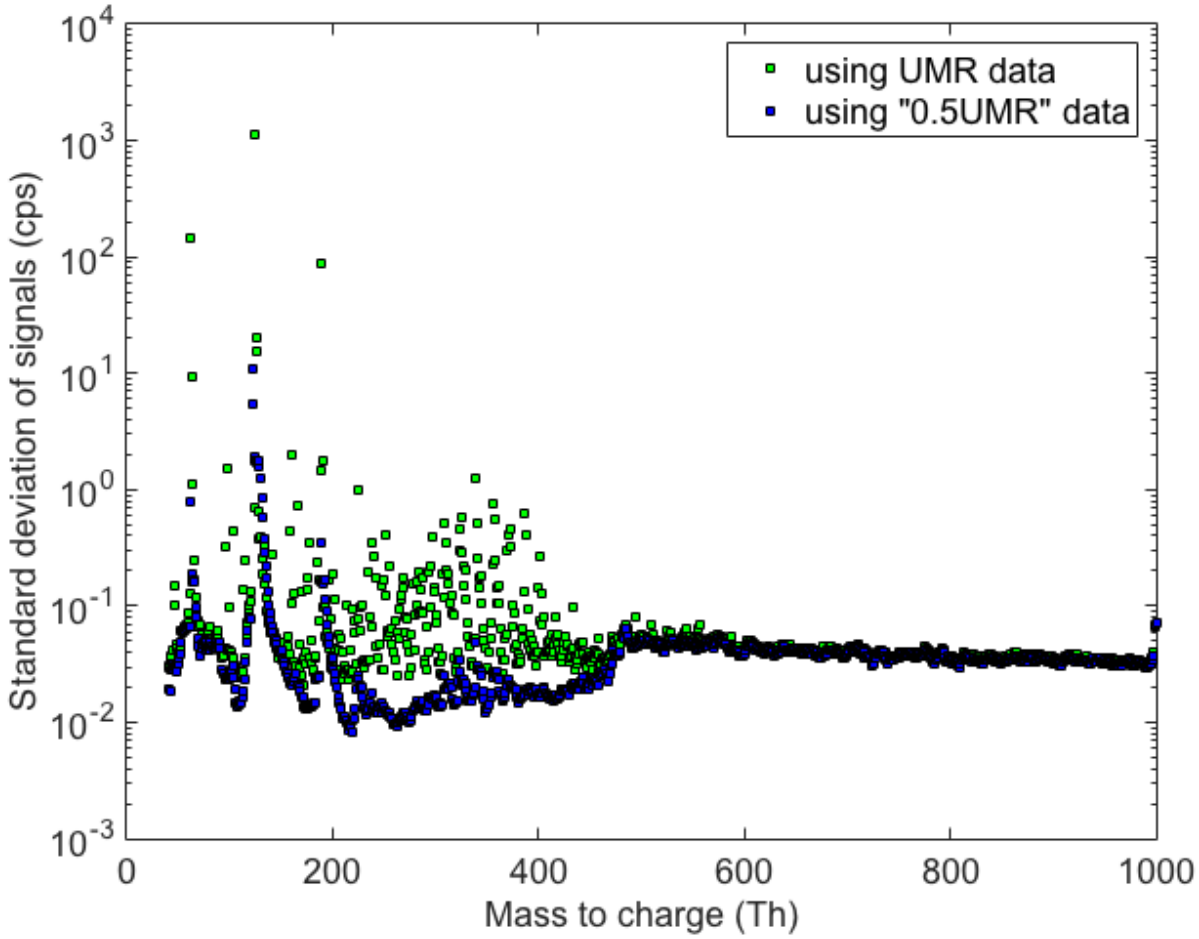

Fig. 2. Standard deviation (1 sigma) of signals using UMR data and "0.5UMR" data.

line 35: eq 6 ??

"Eq. 6" is now replaced by "Eq. 7"

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!?

Yes, this corresponds to moving median over 25 minutes. We will add this information. Choosing the time window width is a tricky question, as the chemical changes do become an issue with too long averaging, but on the other hand taking a median (or average) of 3 points (15 mins) may conversely interpret measurement error (random noise) as chemical change.

Based on our experience, we would not expect chemical processes to cause such radical changes (in form of such peaks or dips that the moving median would miss) to major ion concentrations, in timescales of few minutes. Between the 5 and 7 points windows' there seems to be less variation, thus 5 points was considered to be a solid middle road for this purpose.

We have added a figure (Fig.S6) to the supplement, illustrating this effect and also hopefully clarifying the entire noise estimation method.

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

We have reformulated this sentence.

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

This is also reformulated and expanded on. A figure (Fig. S6) is added to illustrate the assignation procedure to signal bins.

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.

This was indeed a mistake in the text; although the highest 10% of signal was emitted, we still used 10 bins for the remaining data – this is now corrected.

line 73: 940? or 9084/10??

It should be the latter - also corrected this (typo).