

Responses to Reviewers' Comments

We would like to thank the reviewers for their valuable and positive feedback/comments, which helped us to improve the manuscript.

Referee comments are given in black, and our point-to-point responses are in green. Changes made to the manuscript are marked in underlined green. The line number referred here is for the new revised manuscript.

Anonymous Referee #1

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_APITOF 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 variability 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.... "

Response 1.1: We agree with the reviewer. We have revised this part from "In addition, daytime dimer formation (diurnal peak around noon) was identified, which may contribute to NPF in Hyytiälä. Also, dimers from NO₃ oxidation were separated by the sub-range binPMF, which would not be identified otherwise." to

"As two major insights from our study, we identified daytime dimer formation (diurnal peak around noon) which may contribute to NPF in Hyytiälä, as well as dimers from NO₃ oxidation process." in Line 36-38.

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?

Response 1.2: Both Peräkylä et al. (2020) and Bianchi et al. (2019) assess the impact of oxidation on the HOM lifetime, and find that it's negligible under typical conditions. Condensation dominates, even when assuming collision limited reaction with OH radicals. However, for compounds of higher volatility, such as IVOC and SVOC, oxidation could reduce their lifetime. We added the following explanation in Line 87:

“.....which may affect the factor analysis. For compounds of low volatility, such as many HOM, the main atmospheric loss process is typically condensation onto aerosol particles, with chemical sink being negligible (Bianchi et al., 2019). If, on the other hand, a compound does not irreversibly condense, oxidation reactions can also affect its lifetime.”

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

Response 1.3: Ok, we removed this reference from here.

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.

Response 1.4: We agree with the reviewer that different oxidants have their major impacts during different times of a day. Our initial goal here was just to point out there can be at most six pathways to form dimers, if considering the same precursor, formed from the same or different oxidants (O₃, OH, NO₃), so as to remind the readers that molecules from different ranges may have different formation pathways. To minimize the misunderstanding, we modified the sentence into

“..... RO₂+RO₂ reactions (Berndt et al., 2018a;Berndt et al., 2018b). This also means that there can be several different pathways to form dimers from the same precursor VOC, by combining RO₂ formed from the same or different oxidants. As an example of the latter” in Line 124.

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

Response 1.5: For RO₂ + R'O₂ reactions, as reviewed by Orlando and Tyndall (2012) and (Bianchi et al., 2019), there are two main direct RO₂ termination reactions:



Reaction channel (a) will lead to monomer termination products, and (b) will lead to dimer products. It is true that RO₂ + RO₂ forms also monomer products. However, what we specifically meant, is that in this case, the formed monomer does not care about the identity of the other RO₂ taking part in the reaction, other than potentially about whether a carbonyl or an alcohol will be formed (Orlando and Tyndall, 2012). Thus, to a first approximation, in the RO₂+RO₂ terminated

monomer channel, any RO₂ will do as the terminator. This is in contrast with the dimer case, where the identity of both RO₂ will impact the formed dimer. To make it clear, we replaced the sentences in Line 128-133 “Such a molecule will not have a direct equivalent in any of the monomer products, dependent on only one oxidant, which again may complicate the separation of such factors by PMF, if the entire spectrum is analyzed once. However, if separating the monomer and dimer products before PMF analysis, separation of different formation pathways can potentially become simpler.”,

with “Such a molecule will not have a direct equivalent in any of the monomer products: even though monomers can form from RO₂ + R'O₂ reactions, the products from RO₂ are not dependent on the source of the R'O₂. This may complicate the identification of certain dimer factors by PMF if the entire spectrum is analyzed at once, and therefore separation of the monomer and dimer products before the PMF analysis could be advantageous.”

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”.

Response 1.6: We have revised this part in Line 145 from “..... run on the combined ranges. We found that more meaningful factors are separated from our dataset by utilizing the sub-ranges, and believe that this study will provide new perspectives for future studies” to

“..... run on the combined ranges. We found that dimers generated during daytime and dimers initiated by NO₃ oxidation can be separated from our dataset by utilizing the sub-ranges, but not with the full range. We believe that this study will provide new perspectives for future studies”

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

Response 1.7: To make it clearer, we have changed the sentence from “..... Factors 1-3 are all daytime factors, while Factor 4 has a sawtooth shape, which is caused by contamination, mainly by perfluorinated acids, of the inlet’s automated zeroing every three hours during the measurements (Zhang et al., 2019).” to

“..... Factors 1-3 are all daytime factors, while Factor 4 has no clear diurnal cycle, but a distinct sawtooth shape. Factor 4 comes from a contamination of perfluorinated acids, from the inlet’s automated zeroing every three hours (Zhang et al., 2019).” in Line 313-315.

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

Response 1.8: To make it easier to understand, we have changed the sentence from “..... (R3F1_D) basically has no obvious markers in the profile, and as mentioned above, up to ten factors, there would only be more factors fragmented from the previous factor, with similar spectral profiles, but showed different profile pattern with 510 – 560 Th in RCF2_D2 in Range Combined. The factorization of Range Combined was mainly controlled by Range 1 and 2 due to high signals, and the signals in Range 3 are forced to be distributed according to the time series determined by Ranges 1 and 2. Ultimately, this will lead to” to

“..... (R3F1_D) has no obvious markers in the profile. With the increase of factor number (up to ten factors), no clearly new factors were separated in Range 3, but instead the previously

separated factors were seen to split into several factors. However, the spectral pattern in R3F1_D is different from that in the mass range of 510 – 560 Th in RCF2_D2. The factorization of Range Combined was mainly controlled by low masses due to their high signals. The signals at high masses were forced to be distributed according to the time series determined by small masses. Ultimately, this will lead to” in Line 476-482.

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?

Response I.9: (1) As the reviewer suggests, the possible monomers initiated by NO₃ oxidation would have odd integer masses, as listed in Table R1.

Table R1 potential monomers initiated by NO₃ oxidation and their corresponding integer masses

<i>Number of O atom (x)</i>	<i>C₁₀H₁₅NO_xNO₃⁻</i>	<i>C₁₀H₁₇NO_xNO₃⁻</i>
1	227	229
2	243	245
3	259	261
4	275	277
5	291	293
6	307	309
7	323	325
8	339	341
9	355	357

In the monomer range (Range 2), the only night factor (as shown below in Figure R1) is R2F4_N. 325 Th is the highest odd mass in Range 2, with no other significant odd-mass markers. We can do a high-resolution fit to 325 Th, with center mass of 325.06 Th and resolution of 3577 Th/Th, which is quite close to the instrument resolution, ~4000 Th/Th. There can be mainly two candidates for 325 Th, the radical C₁₀H₁₅O₈NO₃⁻ (with exact mass of 325.0651 Th) and monomer from NO₃ oxidation C₁₀H₁₇NO₇NO₃⁻ (with exact mass of 325.0889 Th). In our case, this 325 Th is more likely the radical. In addition, R2F4_N shows significantly higher correlation with ozonolysis dimers (R3F2_N1) (R² = 0.75) compared to the NO₃ oxidation dimer (R3F3_N2) (R² = 0.27). A similar result is also found in the combined range, as shown in Figure R2. We thus conclude that any potential monomer nitrates are minor compared to the non-nitrate monomers, and an instrument with much higher resolution, e.g. the CI-Orbitrap (Riva et al., 2019), would be needed to unambiguously identify such compounds.

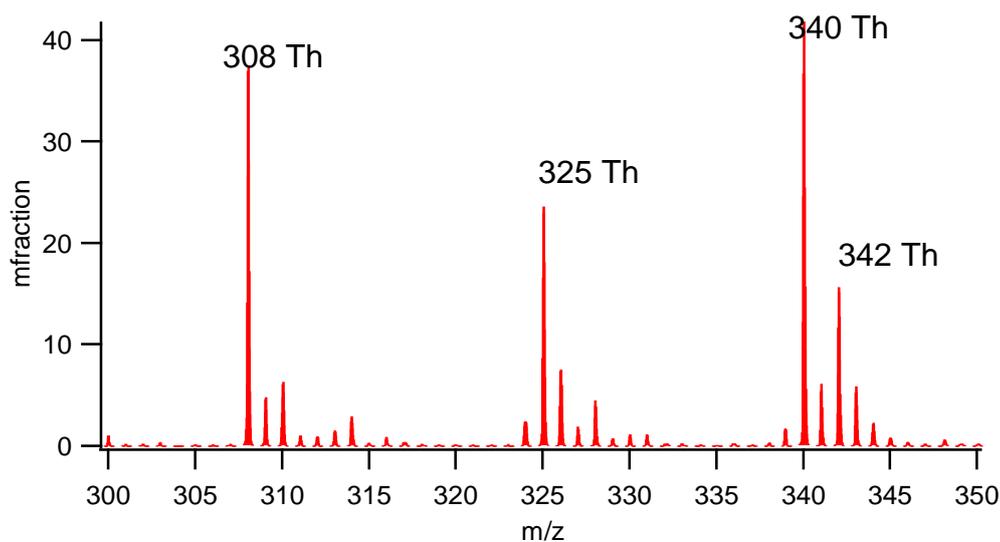


Figure R1 Spectral profile of R2F4_N in fraction, with the main m/z marked

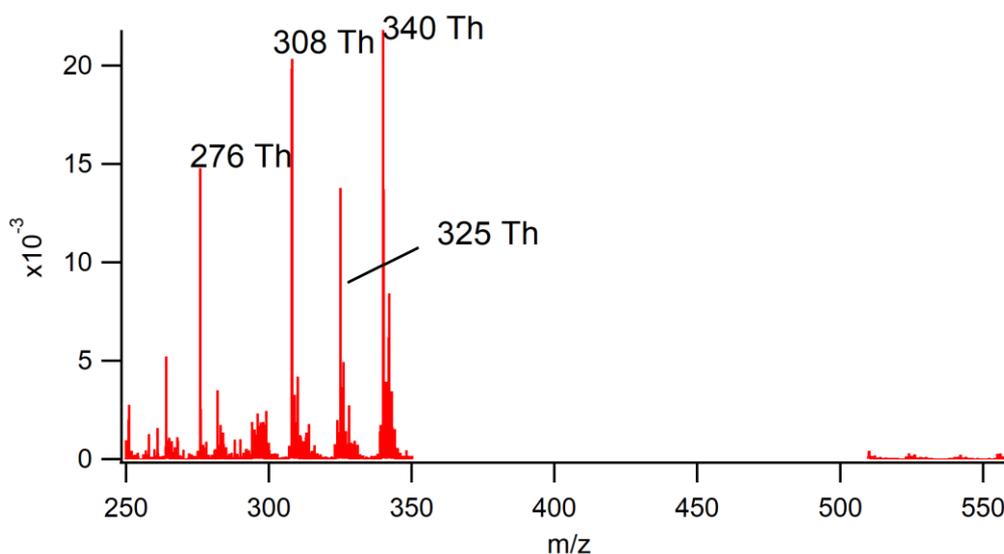


Figure R2 Spectral profile of RCF4_N in fraction, with the main m/z marked in the monomer range

The detection of nitrate dimers of course mean that NO₃-initiated radicals do form efficiently, and participate in the dimer formation by providing the RO₂ supply. We only argue that the potential to undergo autoxidation, and thus form HOM monomers, is limited for the monoterpenes during these measurements. As even less oxidized dimers condense very efficiently, they will have very limited (see also *Response 1.2*) time to react with NO₃ radicals, meaning that it's unlikely that the observed nitrate dimers would be formed from a reaction between nitrate radicals and non-nitrate dimers.

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).

Response 1.10: We agree with the reviewer, and have moved most of the text of this part to supplement. Only the results, discussions of low correlations between different contamination compounds, and indications of volatility effect on factor analysis were kept.

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.

Response 1.11: Thanks for the comments. (1) For the “4. Discussion” part, we adjusted and revised the structure of this part, and rearranged and added the relative contents in different sections, respectively. The previous structure in the “4. Discussion” was:

“4. Discussion
4.1 Comparison of different ranges
4.1.1 Time series correlation
4.1.2 Daytime factor comparison
4.1.3 Nighttime factor comparison
4.1.4 Contamination factor
4.2 Atmospheric insights
4.2.1 Daytime dimer formation
4.2.2 Dimers initiated by NO₃ radicals”,

while the new adjusted structure is

“4. Discussion
4.1 Time series correlation
4.2 Daytime processes
4.2.1 Factor comparison
4.2.2 Daytime dimer formation
4.3 Nighttime processes
4.3.1 Factor comparison
4.3.2 Dimers initiated by NO₃ radicals
4.4 Fluorinated compounds
4.5 Atmospheric insights”.

(2) Now the section “4.5 Atmospheric insights” was simplified and mainly summarized the key atmospheric insights which have been discussed in more details in sections 4.1-4.3.

“Based on the new data analysis technique binPMF applied in sub-ranges of mass spectra, we were able to separate two particularly intriguing atmospheric processes, the formation of daytime

dimers as well as dimer formation involving NO_3 radicals, which otherwise could not have been identified in our study.

With a diurnal peak around noon time, the daytime dimers identified in this study correlate very well with daytime factors in monomer range. Strong correlation between this factor and solar radiation indicate the potential role of OH oxidation in the formation of daytime dimers. By now, very few studies have reported the observations of daytime dimers. As dimers are shown to be able to take part in new particle formation (NPF) (Kirkby et al., 2016), this daytime dimer may contribute to the early stages of NPF in the boreal forest.

The second process identified in our study is the formation of dimers that are a crossover between NO_3 and O_3 oxidation. Such dimers have been identified before (Yan et al., 2016). However, we were not able to identify corresponding HOM monomer compounds. This finding indicates that while NO_3 oxidation of the monoterpenes in Hyytiälä may not undergo autoxidation to form HOM by themselves, they can contribute to HOM dimers when the NO_3 -derived RO_2 react with highly oxygenated RO_2 from other oxidants. Multi-oxidant systems should be taken into consideration in future experimental studies on monoterpene oxidation processes.”

(3) To elaborate the results more, we also added more discussion by including NO_3 radical measurements in the same IBairn campaign by Liebmann et al. (2018), in section 4.3.2 in Line 548-572, as follows:

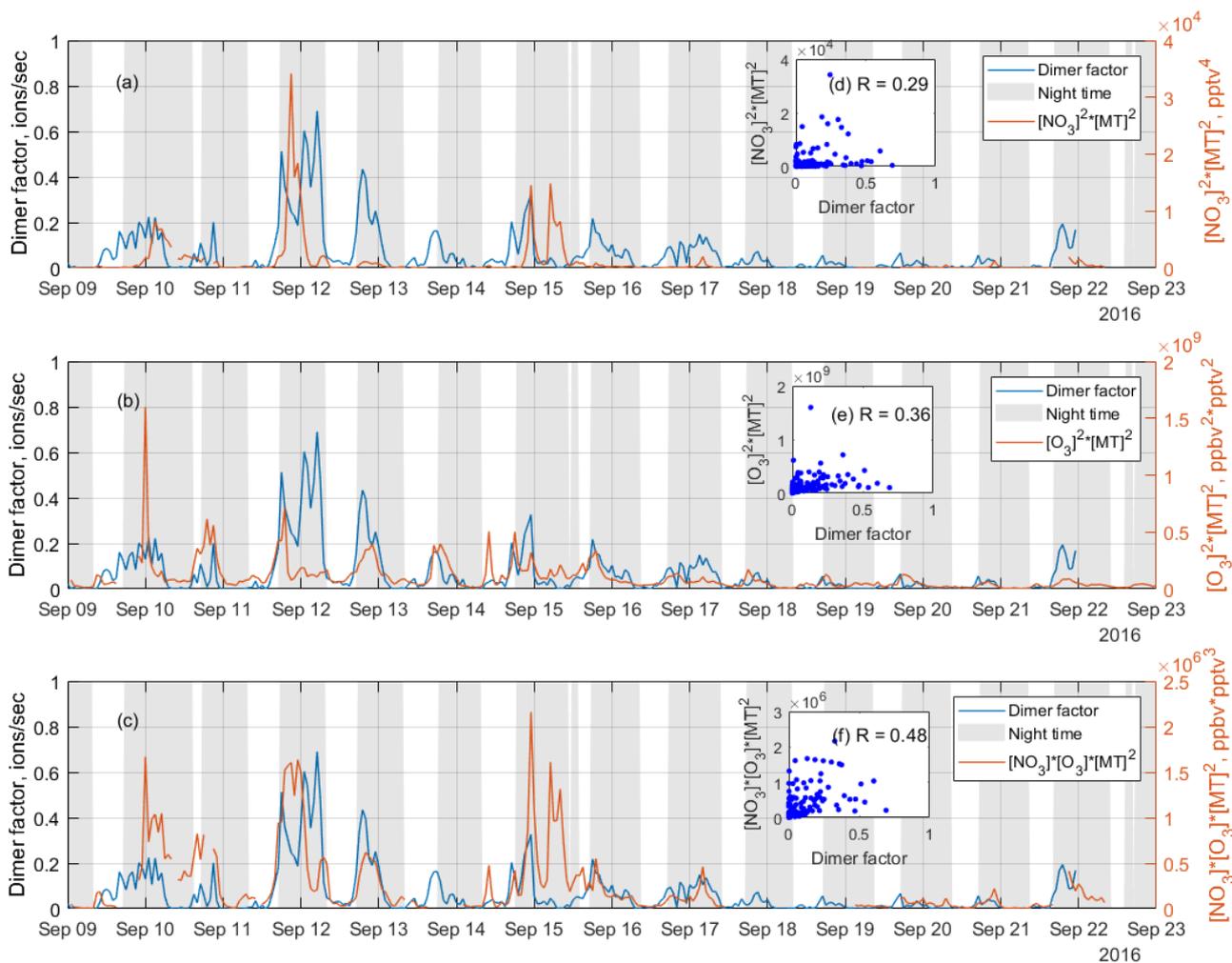


Figure R3 (Figure 7 in the manuscript) Time series of the NO₃ oxidation dimer factor (blue line), and the product of (a) [NO₃]² × [monoterpene]², (b) [O₃]² × [monoterpene]², and (c) [NO₃] × [O₃] × [monoterpene]², where [] represents concentration in unit of pptv for NO₃ radicals and monoterpene, ppbv for O₃, while the scatter plots are shown as inserts, (d), (e), (f), respectively. The scatter plots and correlation coefficients R are only calculated from nighttime data, which is selected based on solar radiation, to eliminate the influence from daytime oxidation processes.

“..... Thus, while there are to our knowledge no laboratory studies on HOM formation from NO₃ oxidation of α-pinene, a low yield can be expected based on SOA studies.

As discussed above, a dimer factor (R3F2 N2) was identified as being a crossover between NO₃ radical initiated and O₃ initiated RO₂ radicals. Figure 7 shows the time series of this factor, as well as the product of [NO₃]² × [monoterpene]², [O₃]² × [monoterpene]², and [NO₃] × [O₃] × [monoterpene]². These products are used to mimic the formation rates of the RO₂ radicals reacting to form the dimers, either from pure NO₃ oxidation (Fig. 7a), pure O₃ oxidation (7b), or the mixed reaction between RO₂ from the two oxidants (7c). The NO₃ concentration was estimated in Liebmann et al. (2018) for the same campaign. Monoterpenes were measured using a proton transfer reaction time of flight mass spectrometer (PTR-TOF-MS). More details on measurement of NO₃ proxy and monoterpene can be found in in Liebmann et al. (2018).

As shown in Figure 7, the time series of the dimer factor tracks those of [NO₃] × [monoterpene] and [O₃] × [monoterpene] reasonably well, but shows the highest correlation with the product of [NO₃] × [O₃] × [monoterpene]². This further supports this dimer formation as a mixed processes of ozonolysis and NO₃ oxidation. The heterogeneity of the monoterpene emissions in the forest, and the fact that no dimer loss process is included, partly explain the relatively low correlation coefficients. The sampling inlets for PTR-TOF were about 170 m away from the NO₃ reactivity measurement (Liebmann et al., 2018), which in turn was some tens of meters away from the HOM measurements. Thus, this analysis should be considered qualitative only.

The nitrate dimer factor (R3F2 N2) was dominated by the organonitrate at 555 Th, C₂₀H₃₁O₁₀NO₃·NO₃⁻. However, unlike the pure ozonolysis dimer factor which had a corresponding monomer factor

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.

Response 1.12: (1) For the conclusion, as both reviewer suggested, changes have been made to simplify the conclusion and highlight the new findings. The new revised conclusion is as follows:

“The recent development in mass spectrometry, combined with factor analysis such as PMF, has greatly improved our understanding of complicated atmospheric processes and sources. However, one of PMF’s basic assumptions is that factor profiles remain constant in time, yet for atmospheric gas-phase species, reactions and sinks may violate this assumption. In this study, we conducted separate binPMF analysis on three different sub-ranges to explore the potential benefits of such an approach for producing more physically meaningful factors.

With binPMF applied on sub-ranges, our study identified daytime dimers, presumably initiated by OH/O₃ with a diurnal peak at around noon, which may contribute to NPF in Hyytiälä. Also, based on the sub-range binPMF analysis, we successfully separated NO₃-related dimers which

did not have a corresponding monomer factor. The NO₃-related factor was consistent with earlier observations (Yan et al., 2016), but would not have been identified from this dataset without utilizing the different sub-ranges. In future laboratory experiments, more complex oxidation systems may be useful in order to understand the role of NO₃ oxidation in SOA formation. Apart from these two findings, we also find other benefits by applying binPMF on sub-ranges of the mass spectra.

First, volatility affects the PMF results. Different compounds emitted from the same source showed different temporal trends, likely due to differences in volatilities. This increased the difficulties for PMF to separate this source in the combined data set, and the resolved profile was less accurate than that of the sub-ranges. Future studies of gas-phase mass spectra should pay attention to this volatility effect on factor analysis.

Secondly, chemistry or sources contributing to the particular range can be better separated. Only the binPMF analysis on Range 3, where HOM dimers are typically observed, resolved two nighttime factors, characterized by monoterpene oxidation related to NO₃ and O₃ oxidation.

Thirdly, peaks with smaller signal intensities can be correctly assigned. The signal intensities between different parts of the mass spectrum may vary by orders of magnitude. In the combined case, the results were almost completely controlled by the higher signals from smaller masses. The separate analysis on Range 3 allowed the low signals to provide important information. In addition, running binPMF on different separate mass ranges also allows us to compare the factors obtained from the different ranges and help to verify the results.”

(2) Minor figure captions are modified into smaller font size, so as to be better separated from the main text.

line 119: any instead of many ?

Response 1.13: Yes, changed.

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.

Response 1.14: Yes, changed.

Anonymous Referee #2

This manuscript presents binPFM (Positive matrix factorization) analysis results of subranges of mass spectra and combined ranges of mass spectra, respectively. The authors compared the results from three sub-ranges and the combined three, and concluded that the PFM results depended on the volatility of the species that is assumed to be identical among species, the chemistry or source that contributes to a particulate range of species, and the relative abundance of different species. The authors also discussed the potential formation mechanisms of observed species, especially dimers formed from peroxy radicals. Generally this is a very interesting study that clearly shows the potential issue when applying the PMF methods to measurements of volatile organic compound with different volatilities, which is of interest to the atmospheric chemistry community. On the other hand, the manuscript is a little bit too technical for Atmospheric chemistry and physics, but can be revised to

fit. I would recommend publication of this manuscript after the following concerns have been addressed.

1. Overall, this manuscript focuses too much on the method itself but does not put enough weight on the science they have obtained by analyzing the dataset. The current organization is more like an AMT paper instead of an ACP one. The authors are advised to move a certain fraction of the technical part, e.g., the contamination session, into the supplement and expand the scientific findings.

Response 2.1: We agree with both reviewers, and have moved most of the text on contamination factor to the supplement. Quite a lot of revisions and adjustments in the part of “4. Discussion” were made to expand the scientific discussions and findings. Details are referred to *Response 1.11* of Reviewer #1.

2. The texts in the conclusion part are quite redundant and just a repeat of the issues with applying traditional PMF to CIMS data, especially in the first two paragraphs. This part certainly can be rewritten to be more concise and to deliver key conclusions only.

Response 2.2: In the conclusion part, we combined the first two paragraphs into one short paragraph, and also largely simplified other conclusions, as well as highlighting more the new atmospheric findings, as in *Response 1.12*.

3. (Line 121), “six different pathways” would not be the best word, since OH and NO₃ chemistry would not generally happen at the same time. Although OH radicals can be generated from pinene+ozone chemistry at night, the chances for cross reactions of dimers between peroxy radicals formed from OH chemistry and those from nitrate chemistry are just low, in my mind.

Response 2.3: We agree with both reviewers. To eliminate misunderstandings, we have changed the sentence. Detail are referred to the *Response 1.4*.

4. (Line 220-232), a couple of statements should be clarified. There is a statement of a bin width of 0.02 Th (Line 221). On the other hand, authors state “25 bins per unit mass” for Ranges 1 and 2 and “30 bins per unit mass” for Range 3. What caused the difference? Also, I assume that a larger range of signal region for Range 3 in further analysis was due to a worse shift in mass-to-charge? Lastly, what is the setup for the combined range analysis?

Response 2.4: Thanks for the comments. (1) The bin width in this study is 0.02 Th. To eliminate unnecessary computation of masses without any signal, only masses in the signal region (regions containing meaningful signals) were binned. The peaks get progressively wider with increasing m/z ratio, so at the higher masses of Range 3 we used a wider window for the signal. In this study, the signal region for Range 1 and 2 is between $N - 0.2$ and $N + 0.3$ Th, at integer mass N, and $N - 0.2$ and $N + 0.4$ Th for Range 3 (Figure R4). So the bins per unit mass for Ranges 1 and 2 is $0.5 \text{ Th} / 0.02 \text{ Th} = 25$, and for $0.6 \text{ Th} / 0.02 \text{ Th} = 30$ bins.

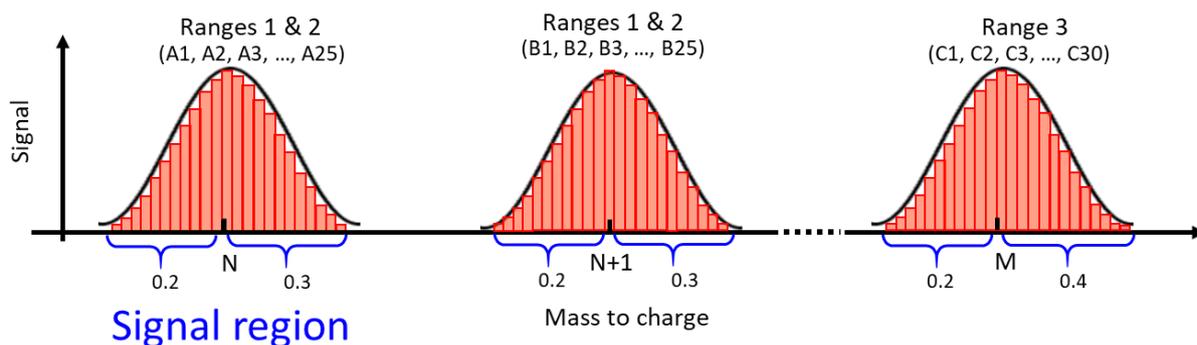


Figure R4 Schematic diagram of data matrix binning process for binPMF analysis. In this study, the bin width is 0.02 Th. For Ranges 1 & 2, the signal region for binning is $[N - 0.2, N + 0.3]$, and for Range 3 is $[N - 0.2, N + 0.4]$.

(2) For the combined range in this analysis, we just combined the mass spectra in the above three ranges, i.e. the three datasets in Ranges 1-3 were combined together to construct combined range. Thus, the highest masses have more bins per integer mass than the mid- and low-mass ranges.

To clarify, we added a statement in Line 240-243:

“To avoid unnecessary computation, only signal regions with meaningful signals in the mass spectra were binned (Zhang et al., 2019). For a nominal mass N , the signal region included in further analyses was between $N-0.2$ Th and $N+0.3$ Th for Range 1 and 2, and between $N-0.2$ Th and $N+0.4$ Th for Range 3. The wider signal regions in Range 3 is due to wider peaks at higher masses. The data were averaged into 1-h time resolution and in total we had 384 time points in the data matrix.”

5. (Sessions 3.2-3.5), since the authors started from two factor analysis to more factors, point out the sequence of factors presented does not necessarily correspond that in the figures in each session.

Response 2.5: We added two sentences in section 3.1 to clarify this.

“..... separately for each Range (sections 3.2 – 3.5). It is worth noting that the factor order in factor evolution does not necessarily correspond to that of the final results. The factor orders displayed in Figures 2-5 have been modified for further comparison between different ranges. More detailed” in Line 288-290.

6. (Figures 2-5), state the time period for the factor contribution.

Response 2.6: The factor contribution is an average from the whole measurement period. For the text, the relative sentence was modified in section 3.2-3.5, respectively, to make this clear.

“..... for further discussion, and Figure 2 shows the result of Range 1, with spectral profile, time series, diurnal cycle and averaged factor contribution during the campaign.....” in Line 313.

“..... Figure 3 shows four-factor result of Range 2, with spectral profile, time series, diurnal cycle and averaged factor contribution during the campaign.” in Line 348-350.

“.....goal in this study. Figure 5 shows the four-factor result of Range Combined, with spectral profile, time series, diurnal cycle and averaged factor contribution during the campaign. The signals in.....” in Line 394-395.

Figure caption in Figure 2-5 were also modified, from “(2) factor contribution” to “(2) averaged factor contribution during the campaign”.

7. (Line 361-362, 455-456), isn't it true that the ultimate source of NO during daytime is still emission?

Response 2.7: Yes, the reviewer is partly correct.

On one hand, the natural source of NO is from lightning stroke, while the anthropogenic sources can be from human activities involving high temperatures, like combustion of fossil fuels.

On the other hand, the monitoring site in this study where we collected the data, Hyytiälä, is located in a boreal forest, with minor anthropogenic emissions (Heikkinen et al., 2019). Nearby sources are two saw mills and a pellet factory 6-7 km away (Äijälä et al., 2019), with no significant emission of NO. The dominant influence of air pollution are still coming from transport from industrialized areas over southern Finland, Russia and the Baltic countries (Riuttanen et al., 2013;Heikkinen et al., 2019). Primary emissions of NO from fossil combustion processes are not long-lived enough to be transported long distances. NO can react with O₃ rapidly to form NO₂, typically on the timescale of minutes. As a result, even though we cannot totally rule out the primary emission of NO during daytime, the photochemical reactions will play the dominant role in NO production. To make the statement more rigorous, revision were made in Line 388:

“During the day, photochemical reactions as well as potential emissions increase the concentration of NO, which serves as peroxy radical (RO₂) terminator and often outcompetes RO₂ cross reactions in which dimers can be formed (Ehn et al., 2014)”,

8. (Line 435), the termination of one peroxy radicals with another does not necessarily have to lead to the formation of dimers.

Response 2.8: As we responded in *Response 1.5*, we agreed with the reviewer that termination of two peroxy radicals doesn't necessarily lead to dimer formation. To clarify the statement, we made revision to the sentence in Line 462-463 to

“This termination step is mutually exclusive with the termination of RO₂ with other RO₂, which can lead to dimer formation.”

9. (Line 497-499), rephrase the sentence.

Response 2.9: The sentence has been removed from the text, to decrease the discussion part of contamination factor.

10. (Session 4.2.1) Although there might not be a daytime factor previously, it is not surprising that dimers are formed in the day. NO channel competes with the self reactions of peroxy radicals but which level of NO will really dominate is still an open question.

Response 2.10: We agree with the reviewer that dimers can be expected to form during daytime, however, the relative studies or results are quite few. For chamber studies, experimental results show that dimer concentration is strongly affected by NO concentration (Ehn et al., 2014). The amount of NO required to hinder dimer formation is also a function of the RO₂ concentrations. In ambient measurement, Mohr et al. (2017) reported a clear diel pattern of dimers with maximum after noon, which is among the first daytime gas-phase dimer observations in the atmosphere, in contrast to the typical daytime minima observed in Hyytiälä (Yan et al., 2016). The NO channel suppresses RO₂ + RO₂ reactions in daytime to a large extent, which leads to lower signals of these daytime dimers to be detected. But definitely, more evidence and studies are needed to reveal and quantify the NO competing ability towards dimer formation in the daytime.

Reference

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