Comments to Reviewer # 1:

We appreciate the comments of the reviewer. Please find a detailed reply to all issues.

The authors perform PMF analysis on 7 years of in-situ, daily NMHC measurements from a site in Southern Germany. They perform some tests of the PMF model assumptions to evaluate the robustness of the results and the appropriate number of factors they use. They interpret the resulting factors qualitatively in terms of a combination of source profiles and compound lifetimes.
It appears the main findings are 1) the PMF analysis leads to plausible results that bear a general resemblance to various emission sources; 2) the abundance of the longer lived compounds was higher than the shorter lived compounds; 3) anthropogenic NMHC were higher in winter than in summer; 4) isoprene is higher in summer and has high reactivity.
One could certainly learn something useful with this type of long-term dataset … for instance, emission trends, possible seasonality in emissions for various compounds, etc. But the analysis here doesn't provide any of that. In the end it's not clear that we've learned anything here that wasn't already known. As such I don't believe the paper rises to the level of meriting publication in ACP.

We beg to differ from the assessment that there is basically no new information coming out of this paper:

- *PMF has been applied for NMHC in remote areas in some studies, but so far there has been little to no discussion about the applicability. Our paper is the first to discuss the capability of the PMF method to identify source categories of NMHC in remote areas. The concept of strict source apportionment related to emission factors which requires mass conservation was not used, instead, a new concept of PMF usage for identifying the dominant factors contributing to rural site NMHC observations was proposed, and the factors were related to emission sources and aging.*
- *It is the first discussion of a method suggested by Sauvage et al. (2009) who treated atmospheric chemical processing by adding uncertainties to the PMF model that so far has not been evaluated at other sites. In addition, another method of Yuan et al. (2012) that looks at photochemical aging and influence on PMF results is now included and discussed.*
- *It is the first manuscript on an analysis of a continuous multi-annual dataset of NMHCs for the pre-alpine area of Germany*
- *It is the first receptor model applied for this region and compounds.*
- *It first discusses the seasonality related to OH seasonality and infers information about the seasonality of sources*

We do not yet see the chance to analyze emission trends. A seven year dataset is too short for such an analysis, a much longer time series would be necessary.

We beg to differ on the lack of seasonality. In our opinion, the seasonality has been analyzed and described in quite some detail within the manuscript. Nevertheless, we extended the analysis by following the specific comments below.

Specific comments.

8156, 15 and subsequent discussion throughout the rest of the paper: 'short-lived compounds emitted at constant rates throughout the year … would be factors of about 7 higher in winter than summer'. This will clearly depend on the lifetime of the compound at hand. Later on you apply this reasoning to interpret the seasonal cycle for different compound groups in terms of whether there is

a likely seasonal cycle in emissions (i.e. if the winter:summer ratio differs from 7, which is the OH ratio). This is a nice idea, but what is needed here is a simple box model calculation of the summer:winter ratio you would expect as a function of lifetime, given constant emissions. For instance, later (8160, 26) you apply this reasoning to the "remote" factor. However ethane is the main compound for this factor, and it is almost inert in winter (lifetime 450 days at OH = 1e5 molec/cm3). Clearly the steady-state argument is not valid here. It also seems that this type of analysis is much better suited to the compounds themselves than the factors, because of the dependence on lifetime.
A couple other points to consider for that type of analysis: rate constants also vary with temperature (not just OH); and prevailing transport patterns (i.e. air mass origin) will likely differ seasonally.

We agree that our approach of comparing the annual courses of the factors to the OH concentration was oversimplifying actual processes. We now applied a simple box model as suggested and included temperature dependent reaction rate constants both for OH and ozone reactions. This enabled us to perform a better and more sound interpretation of the seasonality of the factors. The factor seasonality was determined by using the factor-loadings as weights in combined seasonality of all contributing VOC compounds. The advantage of the PMF method and receptor models in general is that no additional meteorological or chemical processing data is needed. The performed interpretation with the OH annual course merely constituted additional support for the interpretation and the results as discussed in the revised manuscript support the results of our original apportionment and the applicability (and limitations) of PMF to rural datasets.

8161, 24: 'long-lived evaporative compounds had factor 7-9 higher mixing ratio contributions in winter than in summer, although their atmospheric turn-over remained the same all over the year'. What is being said here? That alkanes have the same loss rate in summer as winter??

We changed the whole part about seasonality in the revised manuscript; this statement is no longer existent. However, this was a misunderstanding, as it was intended to say that the product of enhanced OH with reduced NMHC in summer yields a constant "turn-over" (= product of OH and NMHC concentration with rate constant) throughout the year.

8146, 10: 'and in particular NMHC' … why in particular? Are NMHC the main category of VOC contributing to ozone production compared to OVOC?

This statement was withdrawn as it certainly cannot be generalized. Among the primarily emitted VOC (as ozone precursors), the NMHC are generally more important than the OVOC, however, in atmospheric chemistry they go through multiple cycles of oxidation with in consequence higher contribution of OVOC to ozone generation. We did not want to go into such details and thus, we changed the text to '…and amongst them NMHC…'

8146, 19: 'expected a strong increase of biogenic NMHC emissions caused by temperature stress' … not clear what the context is here.

'…stress with future increase of global temperatures…' was added to make it clearer.

8146, 'while in urban areas they (biogenics) play only a minor but non-negligible role'. Surely this would depend on the urban area, wouldn't it? What about a city like Atlanta?

We absolutely agree with this statement. Thus, the text has been altered to the following:

'… while in many urban areas they play a minor role due to high amounts of anthropogenic emissions; however, this is highly dependent on the type and location of the urban area. For major metropolitan areas with large anthropogenic emissions (e.g. Houston, Atlanta) a large impact of the highly reactive biogenic VOC on ozone formation and OH chemistry has been shown (e.g. Chameides et al., 1988;

Leuchner and Rappenglück, 2010; Mao et al., 2010).'

8160, 24: 'ethane appears as an indicator for aged air masses'. This is phrased a bit oddly. Surely ethane is present in pretty much all air masses. It's really the absence or low abundance of other (shorter-lived) compounds that indicate aged air masses … only the longer-lived compounds like ethane are left.

We absolutely agree with this statement. But nothing different is stated here. We changed the phrase to make it clearer to '…The high abundance in combination with the lack of shorter-lived compounds were indicators for aged air masses. …'.

8151, 12: 'obtained reasonable agreement' … what does 'reasonable agreement' mean in this context?

There was no mentioning of 'agreement', only 'obtained reasonable results'. But the phrase '…in terms of plausible factor compositions and contributions of the source categories…' was added to make the statement clearer.

8159, 23: 'aromatics possibly had larger fetch areas during winter due to the longer life-times' … why 'possibly'? Doesn't this stand to reason?

We agree. Due to changes in the text this statement does not appear in the revised manuscript.

8154, 12: 'CO is a product of incomplete combustion' … it is also produced photochemically in the atmosphere.

The comment is correct, however, we anyways withdrew this sentence

8154, 14, 'NO and NO2 are mainly emitted by combustion engines' … what about power plants etc?

In Germany, the traffic sector is the dominant source for NOx followed by the energy sector. Going more regional, in Bavaria the contribution of fossil fuel burning power plants is rather small (ca. 20%) and accordingly, only small contribution by power plant to the short-lived NOx exist.

Comments to Reviewer # 2:

This paper utilizes PMF to identify the sources of hydrocarbons in 2003-2009 measured at a rural site (Hohenpeissenberg). This study can be important to help interpretation of the measured data sets and also other remote measurements of VOCs. PMF is a widely used tool to conduct VOCs source apportionment, but PMF results may need to be interpreted with caution. This study aims to explore the possibility of using PMF results at this remote site. It is an important and interesting work, but it cannot be published in ACP before some major revisions are made.

First of all, we like to thank the reviewer for the comments and suggestions.

(1) This paper brings out that PMF assumption is violated at a rural site. The authors also state that photochemical aging of VOCs can distorts PMF results to identify the possible emission sources of NMHCs (Yuan et al., 2012). But the paper did not pay many efforts to discuss this problem. The methods used in Yuan et al. (2012), e.g. contributions dependence with hydrocarbon reactivity, using two profile ratios to derive their photochemical relationship, are not mentioned or conducted at all. It would be interesting whether the methods are useful at this remote site and whether the methods will support the authors' conclusions.

We do not fully agree that the problem of photochemical aging was hardly discussed. However, we performed the methods suggested (Yuan et al. 2012) to see if the method is applicable to this remote site and if an improvement of the interpretation could be achieved.

As we can see from our calculations, the method suggested by Yuan et al. (2012) does not work well with our data. The most important underlying restriction for the application of this method to our dataset is that we cannot calculate photochemical age reliably from the scaling of the ratio of two compounds with different reactivity. For example, suggested ratios such as benzene/toluene, m+p-xylene/benzene, m+p-xylene/ethylbenzene and others yield very large differences in calculated OH-exposure or photochemical age and also in the derived emission ratios. The choice of a single ratio for the determination of the photochemical age seems quite arbitrary for our site. This is due to several properties at the site: we cannot hold the assumption (assumption 4 from Yuan et al. (2012)) that the initial emission ratios of the different contributing sources are constant for all sources or air masses that reach the site that in addition have very different reaction times with OH, since the site is exposed to the impact of many overlying sources in different distances. Thus, it is not possible to separate aging, mixing and source type from one specific ratio.

In conclusion, we see that neither the (already discussed) method suggested by Sauvage et al. (2009) is improving the interpretability, nor the photochemical age-based parameterization method suggested by Yuan et al. (2012) is well applicable for a site like Hohenpeissenberg. Despite that, since the application of PMF to NMHC data at remote sites is a quite new and not well tested approach, we included a new section in the supplement (S6) discussing the applicability/restrictions of the Yuan et al. (2012) method.

Yuan et al. (2012) suggest other methods to test, if the PMF factors are independent from each other in regard to aging and would thus be 'age factors' rather than source profiles. The first test is for dependency of the factor fractions of the respective factors to the k(OH) values, the second one tests, if one factor is derived from photochemical aging of another one (Fig. S7). Within the two evaporative categories (short-lived and long-lived) and also the two combustion categories (short-lived and residential heating/long-lived) a split of short and long-lived compounds could be observed between the two respective factors (Fig. S6). Not a clear photochemical relationship, as shown by Yuan et al. (2012) for Beijing data, could be seen in the Hohenpeissenberg analyses. The factors discussed here showed a certain separation by photochemical processing into short and long-lived factors, but were still separated into the source categories evaporative and combustion, supporting the source *apportionment from section 3.2. Both tests did not show clear signs of photochemical relationship between the different extracted profiles. As has been discussed before, this is attributed to the complex situation of multiple sources with different transport times overlaying in the receptor profiles. This supports our interpretation of the factor profiles as differently aged profiles of two different source categories (evaporative and combustion) plus a background factor and a biogenic one. We included this analysis in the supplement (section S6).*

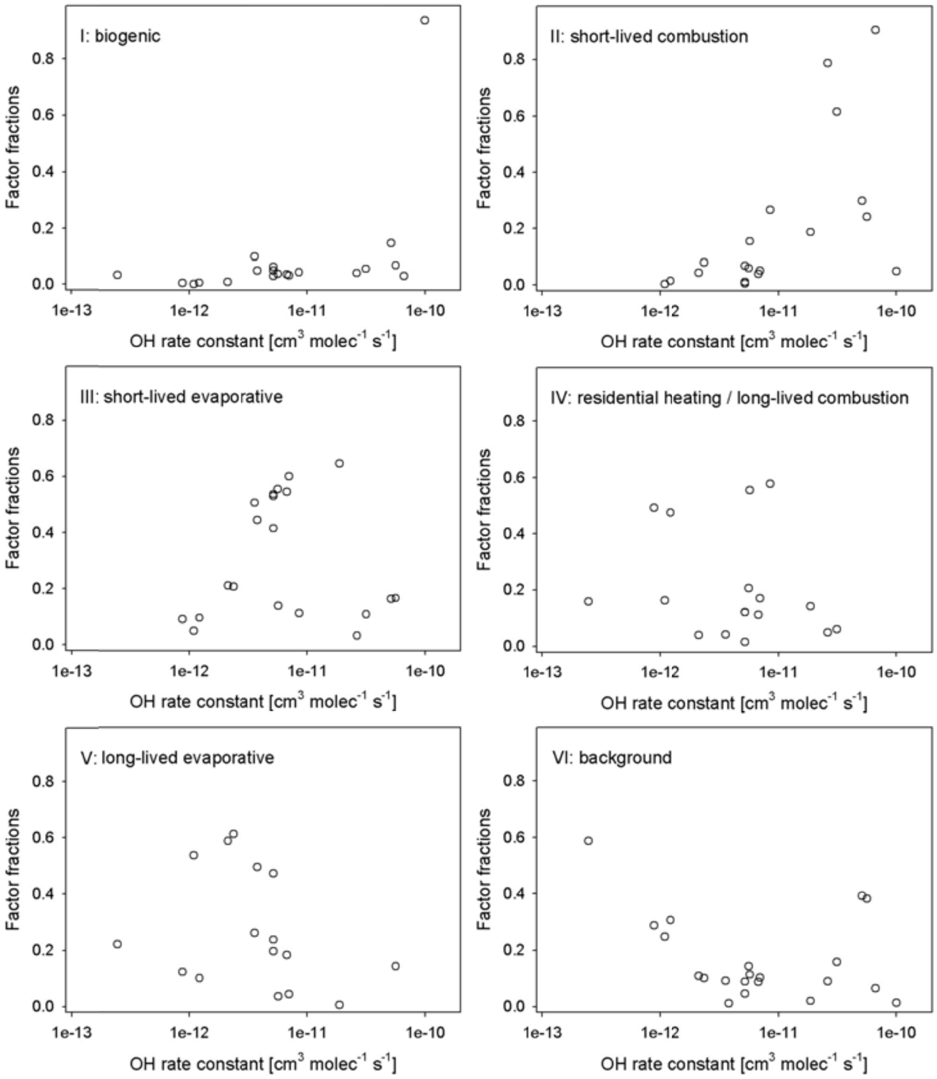

Figure S6: Factor contributions to each NMHC species as a function of its k_{OH} value. Each data point represents one compound. No dependence on k_{OH} can be seen. Within the categories "evaporative" and "combustion" a split of short and long-lived compounds can be observed, but not a photochemical relationship as necessary, if the factors would all be derived from one source category at different photochemical stages.

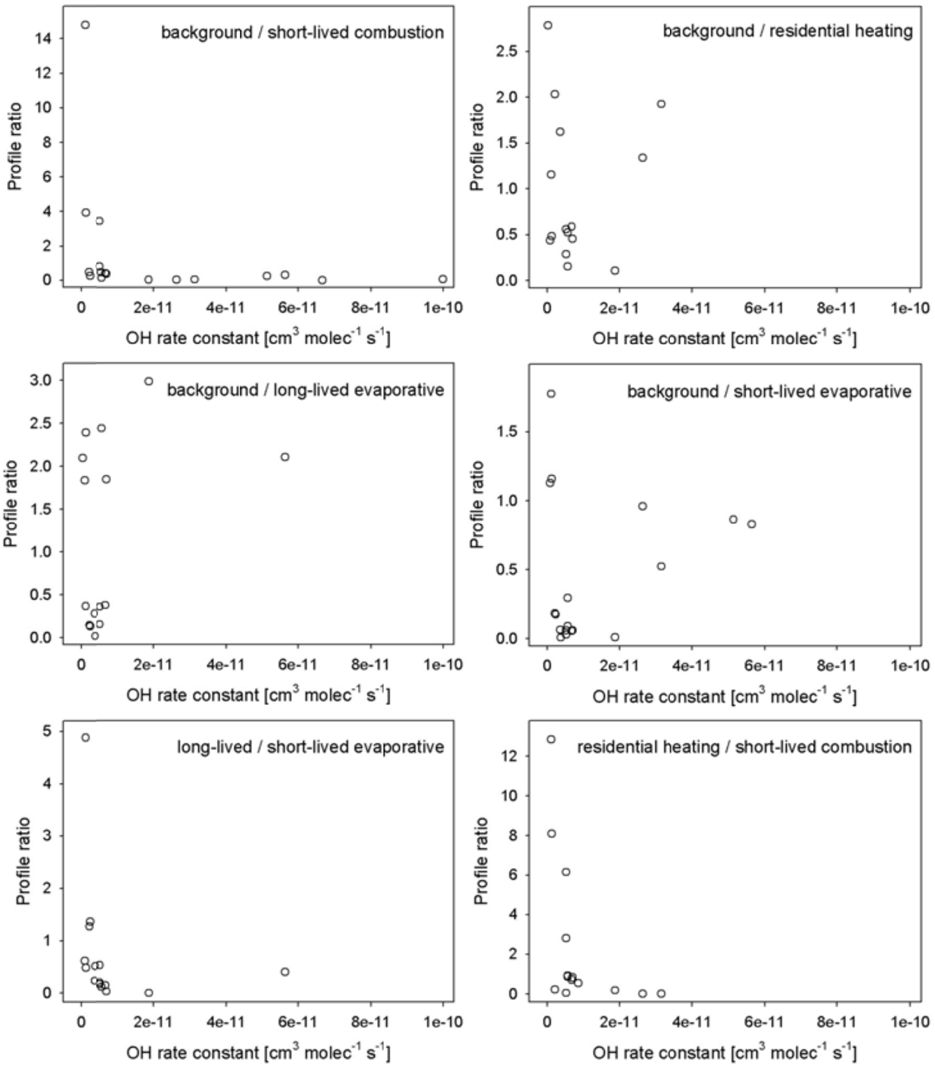

Figure S7: Abundance ratios of the compounds from two profiles as a function of k_{OH} values. Upper left: remote factor / short-lived combustion factor; upper right: remote / residential heating - long-lived combustion; middle left: remote/long-lived evaporative; middle right remote / short-lived evaporative; lower left: long-lived evaporative / short-lived evaporative; lower right: residential heating - long-lived combustion / short-lived combustion; No dependence on k_{OH} can be seen which means that the factors are not derived from each other.

(2) The authors spend several paragraphs in Section 3.2 to describe each factor in detail, which make the reader aware of all of the details. This is the good way to do it. However, Section 3.3 and Section 3.4 provide very little information for the PMF results. These two sections can be both described by one or two sentence. However, this information may be useful for some readers. Thus, it is recommended moving these two sections into supporting information. Thus, it leaves more room for result of other investigations, such as those from comments #1.

Thanks for the suggestions. We moved the respective sections to the supplements.

The 4th paragraph in the conclusion section is very interesting and it should be expanded and included in the discussion part (not just in conclusions).

We decided to keep this part in the conclusions part, updated with the new information gained from the additional tests performed, as a summarizing discussion, but moved some of it into the Results and Discussion section. A whole new revised chapter on seasonality is now included in section 3.3.

(3) The authors only used 13:00 CET measurement data. I am very interesting to see the results of

using only 1:00 CET data or using all of the data. Whether you will see similar factors and similar contributions. Little difference should be expected, since there is not local source even the mixing layer is much shallower in the night.

Other PMF runs with night data only and with combined data were performed in addition. The resulting factors are shown in the supplement and the results are discussed in the main part. The solution for daytime and nighttime data is quasi identical to the daytime data only solution with only decreased contribution of the biogenic factor, as expected. The nighttime data only resembles very well the five anthropogenic factors; it could not resolve the biogenic factor, which is expected.

(4) The two terms "factor profile" and "Contribution of each factor to the species" is better to describe Fig. 1, Fig. 5 and Fig. 7. Also, most of PMF studies normalize the apportioned mixing ratios (left part of Fig. 1) to get the factor profile.

We replaced the terms, although 'source composition profile' is quite common as well. We decided to keep mixing ratios instead of a normalized display, since the profiles stay exactly the same, but have the additional information of the absolute values that make the impact of the single factor compositions visible and allow a comparison between the factors. With the normalized values a comparison to other studies would depend on the species composition and number of species that differs with each study.

(5) Biogenic factor: I agree with you that Factor I is related to biogenic activities, at least partially. Based on the description of this factor, I think two conclusions should be made clearly in the end of the two paragraphs: (a) The factor may represent biogenic sources, but mixing with other sources is also present; (b) If the authors want to use this factor as biogenic factor, the contribution of biogenic source would be overestimated (at least by a factor of 4-5). This overestimate is based on the profile: the factor only contributes 14 pptv of isoprene, but it contributes 49 pptv of ethane. I do not expect 4 times of ethane coming from plant emissions. This may reflect the difficulty of separating biogenic and anthropogenic sources by PMF, as discussed in Section 4.2 in Yuan et al., 2012.

We beg to differ. 34 pptv are contributed by isoprene (not 14) and we also already stated that some contributions of the factor are not purely biogenic. But the discussion was extended to emphasize the possible non-biogenic impact on this factor.

(6) Remote sources: I also agree with the author about this factor. This factor should represent continental background or North Hemisphere background. Is that possible to compare the resolved concentrations with the background values measured at other remote sites (such as in the middle of Pacific/Atlantic ocean).

The most important contributors ethane, propane, acetylene, and benzene agree very well with July and August aircraft data from North Atlantic background air from Lewis et al. (2007). Data for ethane and propane from Pico Mountain, Azores, in the North Atlantic (Helmig et al., 2008) show very good agreement. Ethane and propane data from Mace Head (Yates et al., 2010) are slightly higher on an annual mean than at the remote factor from our analysis, but still in the same range. We added a paragraph to the manuscript to support the remote factor.

(7) I do not totally agree with the authors about the assignment of factors II, III, IV and V. I would think PMF just grouped the species into four different subsets. The lifetime of the four groups are: Factor IV>Factor V> Factor III>Factor II. I think it is fine to define them as short-lived and long-lived, but assigning them into combustion and evaporative sources are ambitious and also meaningless. Some evidence against with the authors' arguments: (a) Both of the two factors (Factor III and Factor V) show some correlation with CO or/and NOx/NOy, indicating some combustion sources are mixed in the two factors. (b) Toluene has similar lifetime as ethene and xylenes have similar lifetime as propene. Toluene and xylenes should also be emitted from vehicles but they are present low in

Factor II, thus Factor II may be just a subset of combustion emissions. Thus, these factors should be assigned to specific sources with caution, until there is more information to support that. The results from Comments #1 may be able to get some insights.

The tests from comment #1 did not reveal a strong photochemical dependency. As you said, we differentiated already into short-lived and long-lived categories. But we still think it is reasonable to categorize those into evaporative and combustion sources since they resemble very well source profiles shown in literature. The interpretation is also supported by the box model results added to the study. (a) We agree that there is some correlation to NO and NO_2 as stated that this comes from medium-lived combustion sources. This of course shows some limitation to totally resolve single sources at this remote site. However, the objective was not the concept of strict source apportionment related to emission factors which requires mass conservation, instead, a new concept of PMF usage for identifying the dominant factors contributing to rural site NMHC observations was proposed, and the factors were related to emission sources and aging. In addition, those correlations with other trace gases must not be overinterpreted and merely give some (limited) additional information, since NO_x also depends strongly on photochemical processes. Correlations can sometimes also have other than physical reasons. (b) Results from the box model support the differentiation into evaporative and combustion sources. We agree that they resemble subsets. If added, Factors II and IV will give a very good representation of combustion sources (that at this site mainly consist of vehicular emissions and emissions from residential heating).

Minor comments: (1) CO is spelled out in P8154 L12, but CO is already present in the above paragraphs. Other species are not spell out. PAN is spelled out in the introduction, but the abbreviation is not shown (P8146 L11).

Thanks, we corrected that.

(2) P8157 L3. 'Relative contributions are the fractions of each substance contributing to each factor" should be "… of each substance attributed to each factor".

Thanks, we corrected that.

(3) Section 3.2.2: What are the meanings of the percentage numbers in the parenthesis.

"fractions of the substance attributed to each factor: [xx]%" added at first occurrence for better explanation.

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Comments to Editor:

My understanding is that HPB has a rather extensive set of other chemical measurements in addition to the 24 NMHCs you analyze here. I would urge you to include some of those parameters in the PMF if at all possible. I am thinking now of NOy, PAN, CO, Radon, and perhaps compounds like CH3CN and acetone, if available. As it is, some are discussed only after the PMF, which seems to me to be much less objective and rigorous.

We included the following substances in the PMF together with the 24 NMHCs (only single substances added as well as combinations of different substances; see manuscript for details): NO, NO_2, SO_2, CO, NO_y, O_3, PAN, PM10, PM3, and black carbon. Not a whole lot of new information could be drawn out of those analyses. However, we included the relevant parts in the revised manuscript, in particular in section 3.2 Source apportionment. The results, when including other substances in the PMF actually were quite similar to the pure correlations of the PMF factors with the trace gas concentrations. That in our opinion is a good sign that the PMF results are quite robust.

Also, I agree with Reviewer 2 as you do in your response, that VOC aging should be explicitly included using the method of Yuan et al., 2012. The method of accounting for reactivity that you have chosen suffers from a lack of knowledge of the starting concentration, an approach using VOC ratios can get around that. As you do this, is would be good to update some of the references on emissions profiles, for example, aromatics in vehicle exhaust have changed in the past 10 years.

We tested the method of Yuan et al. (2012) for photochemical aging in detail as well as performed the tests for photochemical independence of the factors from the same paper. Please see answer to Reviewer #2 and the revised manuscript for details. We updated some references on emission profiles. Overall, our conclusion is that the Yuan method is not appropriate (too many small and disperse sources), however, the PMF yields very useful factor information enabling a characterization of the chemical regime at the station by means of various source category and aging impacts.

We also added a whole new section about seasonality and the usefulness for interpretation of the factors by the application of a box model and comparison of measured and calculated amplitudes according to the reviewers' comments.