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).*

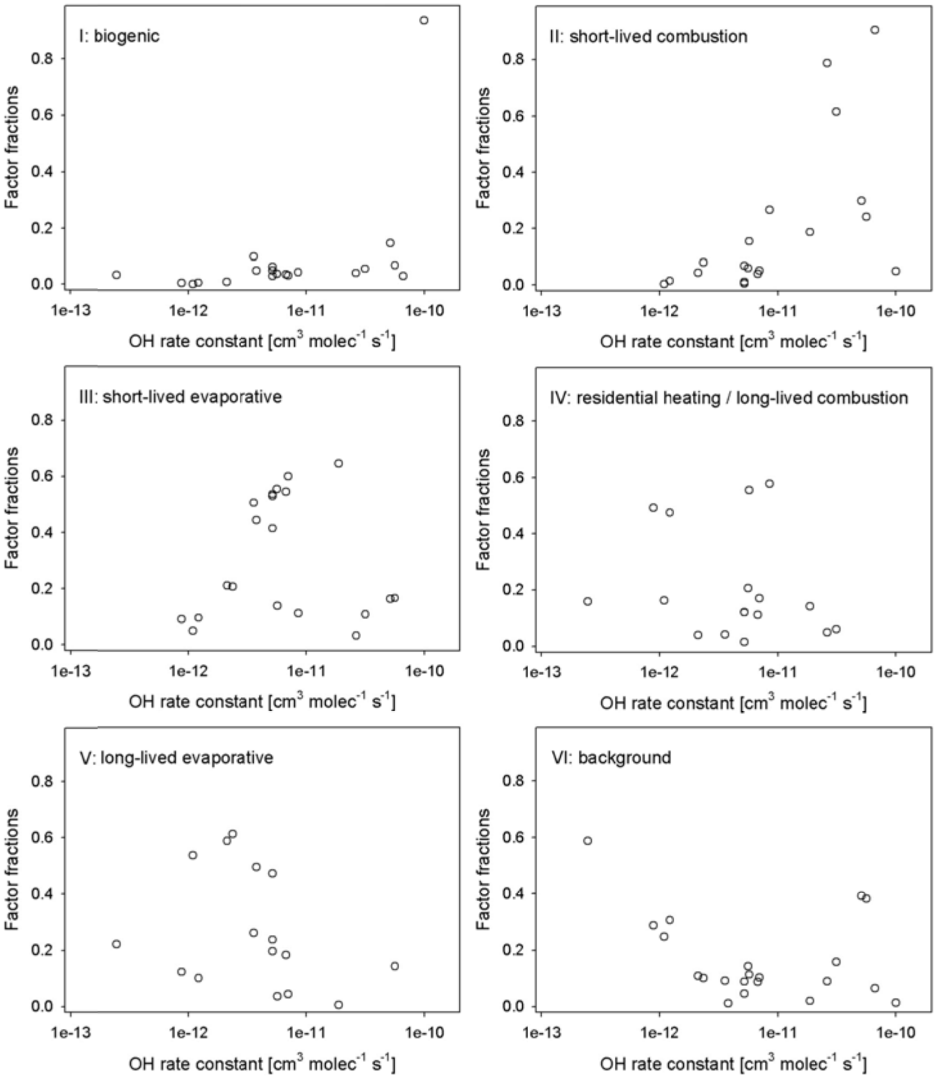

Figure S6: Factor contributions to each NMHC species as a function of its k_{OH} value. Each data point represents one compound. No dependence on k_{OH} can be seen. Within the categories “evaporative” and “combustion” a split of short and long-lived compounds can be observed, but not a photochemical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

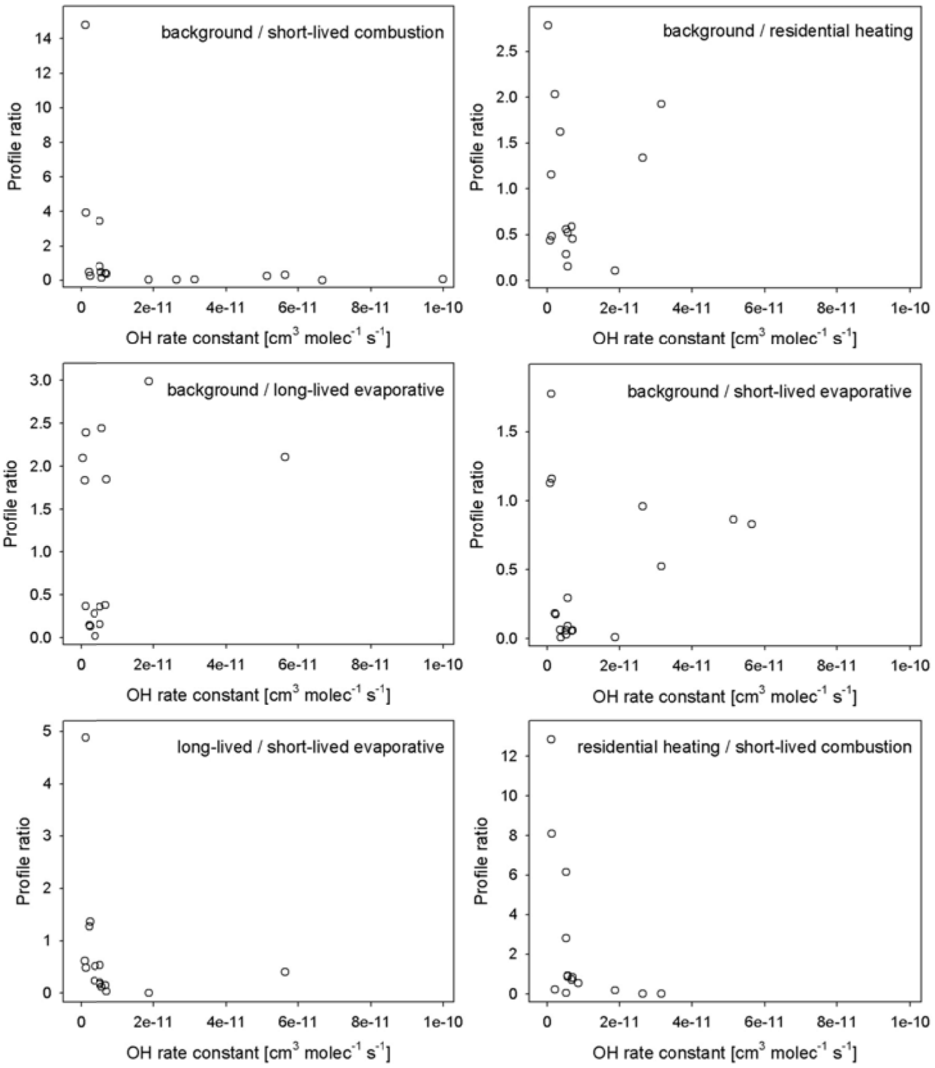

Figure S7: Abundance ratios of the compounds from two profiles as a function of k_{OH} values. Upper left: remote factor / short-lived combustion factor; upper right: remote / residential heating - long-lived combustion; middle left: remote/long-lived evaporative; middle right remote / short-lived evaporative; 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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