Answers to Referee 1

General comments:

There is a very fundamental problem with the entire technique relating to the data model that is employed when combining the two instruments. The standard receptor model employed with PMF requires fixed-profile factors, therefore any combined AMSPTRMS factors must strictly covary for them to be derived as factors. While this will not be an issue for most primary factors (providing the respective lifetimes of the particle and gas phase markers are both long enough that the receptor measurement is representative of the source), one would not expect explicit covariance for secondary aerosol and gas-phase oxidation products in general. Firstly, the different oxidation products in both the gas and particle phase are likely to be produced and consumed on different timescales, which will mean their time series will not necessarily match up. Even if the AMS and PTR-MS simultaneously measure SV-OOA component that is in dynamic equilibrium with the gas and particle phases, the exact proportion that exists within the two phases will vary with ambient temperature, which will remove covariance between the two instruments whenever the temperature changes (e.g. between day and night). This is not to say the technique of combining the two instruments is not of use (this paper shows it clearly is), but it is fundamentally limited and the authors should include more discussion of the data model when introducing the technique. This is particularly important given the prominence SV-OOA is given when discussing the motivation for the work. This also has implications for the interpretation of the relationships found; see specific comments for more detail.

We agree with the comments of the Reviewer about the limitations of the source apportionment approach used here. The combined gas-particle phase source apportionment is very critical since it involves species with different lifetimes and dynamic processes. This approach is suitable for a clearer identification of primary sources, by including primary co-emitted gas-phase pollutants. This was clearly shown in our case for the winter dataset where BBOA was better separated from SV-OOA, which allows a more accurate quantification of the contribution of both primary and secondary fractions.

On the other hand, secondary gas and particle phase species form and decay at different timescales; hence we agree that their covariance does not allow a discrimination between different secondary sources, but may be rather used to infer the formation timescales and lifetimes of OOA species. A precursor concentration can be low because there is little emission of it or because it has high reactivity. In the first case the condensed species would be low, while in the second case the condensed species would be high. Such methodology has been successfully used on numerous occasions (Slowik et al., 2010; El Haddad et al., 2013), which gave valuable insights into the formation and aging processes of OOA.

The Reviewer mentioned that the AMS and PTR-MS could simultaneously measure an SV-OOA component which is in dynamic equilibrium with the gas and particle phases and that the exact proportion existing within the two phases will vary with ambient temperature. However, we do not fully agree on this point since PTR-MS species are

highly volatile and would not significantly partition into the particle phase. Therefore the temperature has no effect on the variability of PTR-MS species via particle/gas phase partitioning.

In the corrected version of the manuscript, we added the following sentences to clarify the limitations of our approach:

Page8561, line 14:

"However, a combined gas-particle phase source apportionment is a critical technique since involves species with different lifetimes and several dynamic processes. This approach is suitable for a clearer identification of primary sources, where particulate and gaseous pollutants are co-emitted. On the other hand, secondary gas and particle phase species form and decay at different timescales; hence their covariance does not allow discrimination between different secondary sources, but may be rather used to infer the formation timescales and lifetimes of OOA species. A precursor concentration can be low because there is little emission of it or because it has high reactivity. In the first case the condensed species would be low, while in the second case the condensed species would be high. Such methodology has been successfully used on several works (Slowik et al., 2010;El Haddad et al., 2012), which gave valuable insights into the formation and aging processes of OOA.
Finally, a cleaner separation of primary sources by using a combined gas-particle phase source apportionment allows also a better separation of secondary sources (as demonstrated in our work for the winter case where the SV-OOA component is completely separated from the BBOA one differently from the PMF_{AMS})."

Specific comments:

- P8533, L5: I note that the error model for the PTRMS does not include a 'minimum error' term. This means that a signal with a low background could have been assigned unrealistically low errors in the low signal regime, which can in turn cause problems for PMF. The AMS gets around this with the use of 'electronic noise' or 'single ion error' terms in its error model (Ulbrich et al., 2009). While I am not saying that this has caused problems here, the authors should comment on what the lowest values the errors are estimated to be.

We agree with the Reviewer that low signal events might be characterized by small errors which might attribute more weight to these points. For the AMS case, a minimum error is applied in order to reduce the impact of small error points. For the PTRMS measurements we did not introduce a minimum error term, but used the variability of the background signal of each ion (3times the background standard deviation) as a metric for the minimum error (compared with the variable errors). The comparison showed that in most of the cases the background variability was smaller or comparable to the errors. For the summer PTRMS dataset ions at mass 31, 41, 47, 61, 73, 75 and 89 were found to have slightly smaller errors compared to 3 times the background variability, but these errors

had still the same order of magnitude as the background comparison metric. For this reason we did not considered these errors affecting much the PMF solution. For the winter PTRMS dataset, the errors of the ions at mass 45, 47, 61, 63 and 97 were a bit lower than 3 times the background standard deviation (although still comparable). The following sentence was added to the manuscript (page 8544, line 18) in order to comment on the estimation of the minimum error for the PTRMS data:

"Differently from the AMS dataset treatment for PMF, no minimum error was applied to the PTRMS data since for all the variables the corresponding errors were bigger or comparable to three times the background variability."

- P8547, L16: There is a fundamental difference in how delta-E is calculated and the more conventional Q/Qexp parameter, in that with Q, the weighted residuals are squared before being summed. This will have the effect of delta-E placing greater emphasis on the variables with the lower weighted residuals. Given that Q/Qexp is the more commonly used parameter within the AMS community, the authors need to justify why they used delta-E instead of the difference between the two Q/Qexp for the different instruments (after removing the effect of C on the PTR data).

In our approach, we used the delta-E metric to evaluate whether the AMS and PTRMS were equally represented by the model. We based our choice on the previous work of Slowik et al (2010). The difference between delta-Q/Qexp and delta-E is that the former considers the squared weighted residuals whereas the latter considers only the weighted residuals. Both parameters allow defining a scaling value C, which will rescale the errors of one instrument before running a new PMF experiment. This would affect the choice of the C-value, without influencing the algorithm in finding the solution.

- P8552: Another reason for the lack of PTRMS tracers for COA may be that there is a mismatch between the lifetimes of the particulate and gas phase tracers, perhaps caused by the COA being semivolatile. See general comments.

Although we agree with the Reviewer concerning his general comments, here we believe that PTRMS markers for cooking were missing or non-recoverable in our PTRMS dataset. As mentioned earlier, the PTR species included in the PMF as tracers are all highly volatile and are expected to remain in the gas phase under atmospheric conditions. Therefore, it is highly unlikely that we don't detect COA gas phase species because of their partitioning between the particle and the gas phases. On the other hand, as cooking is rather a local source, we also don't expect that COA gas phase species would be reacted away, especially during night-time. So, while we agree with the Reviewer that a lot of the variability in the gas phase species might stem from their lifetimes, we believe that primary local gas phase emissions, such as those from cooking processes, if significant, should be detectable in the PTR-MS.
Finally, primary cooking emissions are characterized by the co-emission of gas and particulate pollutants which will be characterized by two peaks corresponding to the meal hours (both for the aerosol and gas phase). The analysis of the diurnal pattern of each

PTRMS ion showed the lack of a cooking-related diurnal, justifying our interpretation of missing cooking traces in our PTRMS dataset.

- P8557, L22: The difference between LV-OOA and SO4 is initially stated to be because of differences in regional sources, so there is no need to invoke local sources to explain the differences in the diurnal profile. The diurnal trend for LV-OOA is quite subtle compared to the others, so is probably not statistically significant compared to the changes in airmass. The comment about local sources should probably be removed. Additionally, when showing diurnal profiles, the authors should specify whether they are using medians or means.

We agree with the Reviewer's opinion regarding the impact of regional sources on the LV-OOA diurnal pattern. However, as we could not exclude a partial contribution to LV-OOA from primary sources, both explanations are presented in the manuscript.
In the caption of figures SI-2.1 and SI-2.2 it is already stated that median values are plotted as diurnals.

- P8558, L27: I would tone down the comment regarding the source of MOA, as this is currently a contentious topic and would require further proof before it can be stated as fact (although this work will undoubtedly contribute to overall understanding). Recommend rewording "due to" to "possibly due to"

"due to" was replaced with "possibly due to" in the manuscript.

- P8560, L3: I would argue that the separation of the two SV-OOA factors is more or less expected, given that the temperature will cause the profile to change with respect to the two phases (see general comments). This being the case, it cannot be argued that this is solely due to different formation mechanisms; the two factors derived could just be two endpoints within the continuum of the temperature-dependent partitioning of the same collective 'SV-OOA' existing in both night and day. This SV-OOA could have been produced from a single source and the two factors are merely a manifestation of the effect of temperature on the partitioning (note that in this context, SV-OOA represents an ensemble of species with different volatilities, so changes in the mass spectra with partitioning are also expected). While there is a relationship between the daytime SVOOA and biogenic emissions, this is not necessarily causal; both the repartitioning of SV-OOA and biogenic emissions are directly linked to temperature, so the correlation in itself does not prove the daytime SV-OOA is produced from biogenics. I should stress that I do not want to devalue the importance of the observations presented, but that there could be a range of explanations beyond those offered by the authors, so they should be more cautious when discussing them.

We rephrased the part about the SV-OOA origin in the manuscript as following:

"A local semi-volatile OOA (SV-OOA) was previously identified by the PMF-AMS analysis (Crippa et al., 2013b). However, this factor appeared to be the product of two

different processes: a temperature-driven partitioning and production during peak photochemistry. By adding the gas phase species into the $PMF_{AMS\text{-}PTRMS}$ analysis, these processes were decoupled yielding two SV-OOA factors: $SV\text{-}OOA_{day}$ and $SV\text{-}OOA_{night}$. On average, $SV\text{-}OOA_{day}$ mass builds steadily during the day, despite the development of the boundary layer, and significantly correlates with ozone and methacrolein + methyl vinyl ketone (m/z 71), short-lived early generation products of isoprene oxidation. This factor can be interpreted as stemming from the production of short-lived secondary organic compounds during peak photochemistry. By contrast, $SV\text{-}OOA_{night}$ contribution is enhanced during nighttime with the temperature decrease and the increase of relative humidity. This suggests that similar to nitrate this factor may be related to the partitioning of semi-volatile SOA into the particle phase."

- P8563, L11: I do not agree with presenting the data in figure 9 as 'source apportionment' of VOCs, due to the lifetime issue given the general comments. For example, benzene is emitted by pollution sources, but it also has a very long atmospheric lifetime (probably longer than HOA), so it is not surprising that there is covariance with factors such as LV-OOA as well as HOA. However, this does not mean that LV-OOA is a 'source' of benzene, this is merely how it is manifested in this particular receptor analysis. As such, I fail to see the value of this figure.

Figure 9 has been removed accordingly with the Reviewer's suggestion.

- Figures: It is odd that the authors should use a combination of stacked bar charts and pie charts when presenting data. Recommend using bars for the sake of consistency and ease of reading.

We decided to use pie charts for Figs. 8 and 9 because they represent more clearly the relative contributions.

Technical corrections:

- P8539, L2: "a predominant" makes no sense. Revise to either "a prominent" or "the predominant"

Corrected with "a prominent"

- P8544, L5: The authors use an uppercase delta for standard error here, but a lowercase in equations 5 and 6. They should make this more consistent.

We do not understand the Reviewer's comment since in equation 5 and 6 no lowercase is used and there is no lowercase delta.

- P8545, L7: Contrary to what is implied here, the PMF2 algorithm natively supports 'robust' mode. While the authors explain what they mean on page 8547, they should clarify the statement here.

The PMF2 algorithm supports the robust mode, however it does not allow one to apply different thresholds to the error matrix when downweighting the outliers. In fact, in a combined PMF approach, the threshold α is different for the AMS and PTRMS since it must take into account the scaling value C applied to the error matrix. This is the reason for using ME-2 and not the PMF2 solver.

- P8546, L5: The mismatch between the instruments is not just to do with SNR; this is already accounted for by the respective error models. This is more likely to do with the relative abundance of covariances (mentioned later) and 'strong' variables within the two datasets.

Sentence at page 8546 (line 5) has been reformulated as following:

"Moreover, when combining two datasets to perform PMF, we must take into account that some instruments have stronger internal correlations within the dataset (e.g. the AMS tends to have characteristic patterns within a single mass spectrum due to the extensive fragmentation associated with the hard ionization (electron ionization)) and that some variables drive the apportionment more than others."

References

El Haddad, I., D'Anna, B., Temime-Roussel, B., Nicolas, M., Boreave, A., Favez, O., Voisin, D., Sciare, J., George, C., Jaffrezo, J.-L., Wortham, H., and and Marchand, N.: Secondary organic aerosol formation from gasoline vehicle emissions in a new mobile environmental reaction chamber, Atmos. Chem. Phys. Discuss., 12, 19769-19797, 2012.

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