Response to Referee #2

General comments

The paper investigates the effects of gas/particle partitioning of semivolatile organic compounds (SVOC) on source apportioning by PMF that incorporates SVOC as input species. SVOCs data in PM2.5 are increasingly used as PMF inputs to apportion organic aerosol sources. The use of particle-only SVOC data in PMF apparently causes complications arising from the strong dependence of their gas/particle partitioning on meteorological conditions (e.g., temperature) and existing particle chemical composition. The paper examines this issue by comparing PMF solutions obtained from particle-only data with those from gas+particle SVOC data. The authors are innovative in deriving the total (i.e., gas+particle) SVOC data from the measured particle-phase concentration by applying G/P partitioning theory. The paper is well-written. The results from this work contribute to improved source identification and apportionment for PM2.5.

Response:

We appreciate the reviewer's reading and valuable suggestions on how to improve this paper. We have considered each comment carefully and given responses below

Major comments:

1. Uncertainty in deriving the gas-phase SVOCs: The authors estimated gas-phase SVOCs using Pankow's absorption partitioning theory. There are studies indicating that adsorption onto solid-like particle surface (e.g., soot surface) also contributes to partitioning of SVOCs (such as PAHs) in particles (e.g., Venkataraman, 1999; Yu and Yu, 2012). Some discussion is needed to address the uncertainty introduced by assuming absorption only partitioning.

Response:

We agree with referee that the adsorption to particle surfaces could play some role in gas/particle (G/P) partitioning of SVOCs (Mader and Pankow, 2002), especially for light components (Yu and Yu, 2012).

In this work, absorptive partitioning was assumed as the dominant mechanism based on previous studies (Liang et al., 1997; Mader and Pankow, 2002). The uncertainties in gas phase SVOC introduced by the missing of adsorptive partitioning were not estimated in this work. However, we will verify and refine the current method for gas phase SVOC estimation by field measurements, and if necessary, include the adsorptive mechanism for gas phase SVOC estimation.

To make it clear, the manuscript will be revised as follows…

Page 5204, lines 4-5, "In this study, gas-phase SVOC concentrations were estimated using their particle-phase concentrations based on Eq. (1)." will be changed into "In this study, gas-phase SVOC concentrations were estimated using their particle-phase concentrations based on absorptive mechanism (Eq. 1). The adsorption of SVOC onto particle surfaces (e.g. soot surface) was not considered in this work. "

Page 5218, line 16, "However, the pre-assumptions (e.g. $\overline{\mathrm{MW}}_{\mathrm{OM}}$ and ζ_{OM} values)…" will be changed into "However, the pre-assumptions (e.g. absorptive partitioning, $\overline{\mathrm{MW}}_{\mathrm{OM}}$ and ζ_{OM} values)…".

2. OC1 fraction is excluded for PMF analysis on the ground that this fraction of OC is semivolatile and the gas-phase concentration of OC1 could not be estimated. It is not clear to me why the authors do not use the entire filter OC as PMF input so that the whole filter OC could be apportioned to sources (or "factors") resolved by PMF. Breaking OC into OC1, OC2, OC3, OC4, and PC and inclusion of the sub-fractions of OC (i.e., OC2 and OC3) do not appear to facilitate source identification by PMF, as shown in Fig. S1. At a minimum, discussion is needed on the PMF solution if the whole OC is used as PMF input instead.

Response:

The primary objective of this work is to eliminate the influence of G/P partitioning on PMF analysis by using total concentrations (particle + gas phase) of each input SVOC species. In this work, a big part of the entire filter OC (OC1, 47.6% on average) is subject to G/P partitioning, and no study has measured or estimated the G/P partitioning coefficient for gas phase OC. The entire filter OC or particle-only OC1 could not be adjusted by G/P partitioning theory in this work, while all speicated particle phase SVOCs concentrations were corrected by adding estimated gas phase concentrations as inputs for PMF analysis. As a result, using particle-only OC1 or entire filter OC as input for PMF will lead to biased source apportionment results compared to using G/P partitioning corrected OC1 or entire filter OC, and we only include those OC fractions (OC2, OC3 and PC) that are less or not affected by G/P partitioning process.

To make it clear, we will change "; and the gas-phase concentration of OC1 could not be estimated due to the complex composition" (page 5207, line 28) into "The gas-phase concentrations of OC1 (or total OC) could not be estimated by using G/P partitioning theory in this work.", and add "Using particle-only OC1 (or total OC) as input for PMF will lead to biased source apportionment results, since all the SVOC compounds were adjusted by adding their estimated gas phase concentrations to measured particle phase concentrations." right after that (Page 5208, line 1) in the revised manuscript.

Given the fact that a big part of EC and OC fractions were lumped in one factor (Bulk carbon factor), the factor contribution time series (Figure S2g) still provide insights on related sources, which is helpful for our future work. The correlations between the factor contributions and ozone concentrations ($r = 0.46$, Table S6) and summer peaks in contribution time series (Figure S2g) suggest that the OC fractions loaded on this factor could be related to secondary organic aerosol (SOA) formation, thus we conclude that more specific source markers (e.g. SOA tracers like 2-methyltetrols) were needed to further apportion the bulk carbon factor. In urban area, EC is primarily from incomplete fossil fuel combustion. The summer peaks of factor contribution to EC should be attributed to the increased EC emission from motor vehicles under higher ambient temperature (Antony Chen et al., 2001).

3. A few unique source tracers, such as cholesterol for meat cooking and methoxyphenols for wood burning, are measured but are not included in PMF source analysis (see Table S2). Why are they excluded? Would not their inclusion help to apportion the bulk carbon factor?

Response:

To compare the PMF results of this work with those derived from particle-only SVOC data set (Xie et al., 2013), candidate input species of this work were selected from the 51 SVOC compounds used in the previous study. In the previous Xie et al. (2013) study, cholesterol was not included in the 51 species for PMF analysis due to low S/N ratio. Including species with low S/N ratios as input for PMF analysis will lead to lower factor matching rate. A high factor matching rate (more than 50%) reflects the uniqueness of base case factors, robustness of the base case solution to input data set (Xie et al., 2012). In addition, the source contributions for meat cooking probably exhibit a winter peak and weekend increase, while the bulk carbon factor has an opposite time series (summer peak and weekend decrease; Figures S2g and S3g). Thus the inclusion of cholesterol will not help to apportion the bulk carbon factor substantially, but make the comparison between current and previous work more complex.

As we mentioned in section 2.4, the criteria for species screening were interpretability and factor matching rate (>50%). Including methoxyphenols for PMF analysis will lead to a factor matching rate lower than 50%. Moreover, the wood burning factor only accounted for 0.16% - 4.21% to reconstructed $PM_{2.5}$ mass in the previous particle only-based study (Xie et al., 2013). Thus the inclusion of methoxyphenols will not substantially help to apportion the bulk carbon factor, but lead to an unstable PMF solution.

4. The PMF solutions are represented as n-alkane, sterane, light SVOC, and PAH factors, instead of pollution sources that these tracers track (e.g., fossil fuel evaporation, vehicular exhaust, etc). Apart from a brief mentioning that the light SVOC factor is associated with fossil fuel evaporation and biogenic emissions, there is no discussion about what are the underlying pollution sources for the other organic marker factors. Although this work focuses on the effects of using particle-only SVOC vs total SVOC data on PMF solutions, the ultimate objective of PMF analysis is to apportion PM2.5 mass or PM2.5 OC into pollution sources, the information that can guide formulation of control strategies. Some elaboration of the associated pollution sources is needed.

Response:

The primary objective of this work is to derive a method to remove the influence of G/P partitioning on PMF analysis, and the current PMF solution might be subject to great uncertainties due to the uncertain gas phase SVOC estimation. Only after the verification or adjustment of the method used to estimate gas phase SVOCs by field measurement, we will be able to relate each PMF factor to specific pollution sources confidently.

In addition, the previous particle only-based study (Xie et al., 2013) has discussed the underlying pollution sources for each factor already, and each factor resolved in this work could be uniquely matched to one factor in the previous study based on factor profile and contribution time series. So we will add "According to the previous Xie et al. (2013) study, the 7 factors in the current work could be primarily or partly related to secondary ion formation (nitrate and sulfate factors), road dust (*n*-alkane factor), lubricating oil combustion (sterane factor), fossil fuel evaporation and biogenic emissions that subject to atmospheric processes (light SVOC factor), motor vehicle emissions (PAH factor) and secondary organic aerosol (SOA) formation (Bulk carbon factor)" (page 5213, line 12) in the revised manuscript, but not discuss the pollution sources associated with each factor in detail.

5. Dominance of odd alkanes (e.g., C31, C33) in the relatively higher n-alkane range is characteristics of vegetative detritus organic aerosol source (Rogge et al., 1993). No odd-carbon dominance is discernible in the n-alkane factor resolved by PMF. Can the authors comment on whether this implies that this n-alkane factor is associated fossil fuel-related sources? Similarly, what are the source implications regarding the strong presence of smaller n-alkanes, oxy-PAHs and C12, C16, and C18 fatty acids in the light SVOC factor?

Response:

As mentioned in the response to comment #4, it is premature to discuss underlying pollutions sources for each factor in detail as we still need verified partitioning parameters; moreover, we have already elaborated possible pollution sources associated with each factor in the previous particle only-based study (Xie et al., 2013). One sentence listing the possible sources associated with each factor based on the previous Xie et al. (2013) study will be added in the revised manuscript. Unfortunately, no additional information could be gleaned from this work regarding specific sources, and therefore we do not include any more discussion on pollution sources in the manuscript.

6. Assuming the PMF solution using total SVOCs as input species are correct, how much does the particle-only PMF solution overestimate/underestimate the individual sources? This information can be extracted in Fig.3, but it is good to describe in words in the text for readers to better comprehend the importance of considering G/P partitioning when SVOCs are used in PMF.

Response:

In Figure 3, higher factor contributions of carbonaceous factors from particle-only solution could be observed compared to those from total SVOC-based solution (Figure 3). This is most likely caused by the omission of OC1 for total SVOC-based PMF analysis, since OC1 accounted for 47.6% of the entire filter OC on average. While the particle only-based study used total OC for PMF analysis. Therefore, Figure 3 does not show any information on the overestimation/underestimation of particle only-based analysis, but the similarity in factor contribution time series between G/P partitioning-corrected and uncorrected solutions.

To make it clear that particle only-based and total SVOC-based PMF analysis use different OC, we will add "(sulfate, nitrate, EC and total OC)" after "Fifty one SVOCs and four bulk speices" in page 5207, line 19, and "While the particle only-based study used total OC for PMF analysis." at the end of section 3.4 (page 5214, line 23).

Minor comments:

1. Page 5212: Please clarify whether "straight OC" includes OC1 and OC4, which were excluded for PMF analysis.

Response:

The straight OC fractions only included OC2, OC3 and PC. We will clarify this in the revised manuscript by adding "(OC2, OC3 and PC)" right after "straight OC fractions" (Page 5212, line 8).

2. Conclusion (Page 5218): Can the authors be more specific in their suggestion for gas-phase OC data? What type of gaseous OC, total or speciated SVOCs or other?

Response:

We appreciate the referee's suggestion. The "gas-phase OC data" (page 5218, line 20) will be changed into "total and speciated gas-phase SVOCs (e.g. *n*-alkanes, PAHs)".

3. Table 1: The last value of MWom should be "300", not "30".

Response:

This will be revised.

4. Tables S1-S4: Please specify whether concentrations of the organic molecular markers are from filter measurements or the sum of measured filter concentration and derived gas-phase concentration.

Response:

We will add "(gas + particle phase)" in the titles of Tables S1-S4 to specify that the organic molecular markers are the sum of measured filter concentration and derived gas-phase concentrations.

5. For figures in supporting document, please do readers a service to include figure captions with their respective figures on the same page for easy reading.

Response:

We appreciate the reviewer's suggestion and apologize for this inconvenience. However, we do believe that the figures are more legible generated as full pages (and thus no room for the figure captions) and prefer to leave them in their current form, with the captions together on a separate page.

References

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