Anonymous Referee #3, 26 Nov 2022

Major comments:

1. ***Lines 165-193 and lines 246-262: I am disinclined to use the label 'I/SVOC-P' since IVOCs (assuming 'I' stands for IVOCs in the label) shouldn't really be in the particle phase. The ratios the authors are using from Lu et a. (ACP, 2020) and likely the other sources are to determine SVOCs only. This issue was raised by referee #2***

Re: Thanks for the reviewer's comments. According to this comment and that raised by referee #2, we have changed the labels of 'I/SVOC-G' and 'I/SVOC-P' to be 'gas-phase' and 'particle-phase'. The labels of 'I/SVOCs-G-to-VOCs' and 'I/SVOCs-P-to-POA' were changed to be 'G-ratio' and 'P-ratio' in the entire text.

2. ***I would recommend the authors use a different name for the 'IMPROVE' simulation since it doesn't convey how it is different from the 'BASE' simulation.***

Re: Thanks for the comments. We have changed the name of 'IMPROVE' to be 'I/SVOC-E' in the whole text.

3. ***Section 3.2.2: This is an important section of the paper, but it seems like the authors overgeneralize the model-measurement comparison and give the model too much credit; I found this to be a common theme in the paper. For instance, while the model holds diurnal trends across seasons, it isn't clear that the observations do the same, particularly in the winter months. It is easy to claim that the 'model works' but it comes at the cost of ignoring useful insight that the comparison sheds.***

Re: Thanks. We agree with the reviewer's comments and make some revisions in the revised manuscript as follows.

Changes in manuscript:

The I/SVOC-E simulation also demonstrated improvements in reproducing the temporal variations of SOA, especially during the daytime (Figure 7e−7h). Compared with the BASE simulation, evident increases in SOA concentrations during daytime can be observed in I/SVOC-E simulation (Figure 7e−7h), which agrees better with the observation. However, the model is still hard to capture the diurnal patterns of SOA observed in most seasons, except for the summer, when both the concentrations and diurnal variations of SOA are well reproduced, which indicates that SOA in summer is mainly subject to photochemical oxidation of I/SVOC emissions, while SOA formation will be largely affected by other factors in other seasons, especially during the nighttime in cool seasons. For example, an increasing body of experimental and observational evidence suggest that heterogeneous and multiphase reactions also played important roles in SOA formation especially during pollution episodes (Guo et al., 2020; Kim et al., 2022). Recent studies also found that nocturnal NO_3 oxidation was also an important route for SOA formation, which would drive the enhancement of SOA during the nighttime (Yu et al., 2019; Decker et al., 2021). Yet mechanism and parameterizations of these processes remain unclear, making the involvement of these processes in the model difficult. In addition, I/SVOC emissions from outside of the YRD region might be underestimated due to the lack of detailed base emission inventory, resulting in the corresponding underestimation of the transported SOA, which were prominent especially in autumn, winter and spring in Shanghai. High-resolution I/SVOCs emissions inventory is urgently needed to be developed at a larger regional scale.

4. ***Too much precision (3/4 significant figures) in the numbers presented in the text?***

Re: Thanks. We have reduced the retained significant figures in the revised manuscript.

5. ***Figure 8: What are the reasons for why the spatial distribution of SOA changes between seasons for the same source? I understand that this could be the case for biogenic VOCs but I am confused why one would expect this for mobile or industrial sources, emissions from which should be less sensitive to seasons.***

Re: Thanks for the comments. The main reason for the spatial difference of each season is the different dominant wind direction. In the Yangtze River Delta region, northwest wind prevails in spring, southeast wind prevails in summer, and northeast wind prevails in autumn and winter. However, in general, the SOA spatial distribution of the same source in different seasons is not very different, which has been explained in the original text.

6. ***While the emissions, chemistry, and SOA potential are much better understood for I/SVOC emissions from mobile sources, that isn't necessarily the case for non-tailpipe sources of I/SVOCs (e.g., solvent use). This needs to be discussed in the final section of the paper.***

Re: Thanks for the reviewer's comments. We have made some revisions for this section in the revised manuscript as follows.

Changes in manuscript:

With the addition of source specific I/SVOC emissions, we successfully quantified the contribution of each source to POA and SOA concentrations in YRD. For POA, cooking emission is the predominant source, which concentrates in urban area of YRD in accordance with the population distribution. For SOA, for the first time, we demonstrate that I/SVOCs from industrial sources are dominant contributor, followed by those from mobile sources. In summer, the contributions of biogenic emission to total SOA are also non-negligible, especially for the cities in southern YRD. Spatial and seasonal variations in the source contributions suggest that control strategies for OA pollution should vary by cities and seasons. For urban area, cooking emissions has been emerging as an important POA source, not to mention their impacts on SOA formation are not yet certain. Our results suggest the control measures on the cooking emissions should be strengthened in the future for the further reduction of POA. Another important source of SOA in urban area is mobile source, especially gasoline and diesel vehicles. Reduction in I/SVOC emissions from vehicles are effective measures in the mitigation of urban air pollution, which is also technically feasible as has been demonstrated in Qi et al. (2021). Continuous improvement in emission standards is one way to promote the reduction of motor vehicle related SOA. Our study further reveals that non-tailpipe sources of I/SVOCs (e.g., solvent use, petrochemical, etc.) are major contributors to SOA formation in the YRD region, consistent with Chang et al. (2022)'s model results in the national scale. However, current understanding of SOA formation potentials from these sources are still far from enough. For example, the localized I/SVOC emission factors and source profiles of these sources are still missing. Their chemical behavior and SOA yields may be different from the emissions from mobile sources which have been widely studied, which urges in-depth studies on these sources as well as the corresponding control measures.

7. ***For referee #2, comment #2, consider the work of Morino and coworkers: https://doi.org/10.1021/acs.est.8b01285 and https://doi.org/10.1016/j.atmosenv.2022.119319.***

Re: Thanks for the reviewer's suggestion. The work of Morino and coworkers is interesting. The work of Morino and coworkers is interesting, which to some extent complements the contribution of stationary source emissions from the industrial and energy sectors to organic aerosols, and improves the simulation of OA in winter. At present, their results cannot be included in the model system in this study, but we discussed them in Section 3.2.2, see the revised manuscript.

Changes in manuscript:

A recent study furtherly found that there were considerable emissions of condensable organic aerosols from stationary sources in the industrial and energy sectors, which would effectively improve the contributions of the industrial sector to OA simulation especially in winter, should also be considered in the future (Morino, et al., 2018; Morino, et al., 2022).

New references:

Morino, Y., Chatani, S., Tanabe, K., Fujitani, Y., Morikawa, T., Takahashi, K., Sato, K., and Sugata, S.: Contributions of condensable particulate matter to atmospheric organic aerosol over Japan, Environ. Sci. Technol., 52, 8456−8466, 2018.

Morino, Y., Chatani, S., Fujitani, Y., Tanabe, K., Murphy, B. N., Jathar, S. H., Takahashi, K., Sato, K., Kumagai, K., and Saito, S.: Emissions of condensable organic aerosols from stationary combustion sources over Japan, Atmos. Environ., 289, 119319, 2022.

8. ***For referee #2, comment #13, consider adding details about the multigenerational oxidation scheme to the methods section.***

Re: Thanks. We have supplemented some details about the multigenerational oxidation scheme in the revised manuscript.

Changes in manuscript:

Multi-generation oxidation was considered by implementing further oxidation of the vapors from the initial oxidation, which redistributes the mass across the volatility bins of C* = 10^{-2} to 10^{2} μg·m^{-3}, and thus fragmentation and functionalization were included. It is worth noting that only one-step oxidation of the vapor products was considered, using the default aging scheme for the oxidation products of POA in the CMAQ (Murphy et al., 2017). Additionally, SOA formation from SVOCs were treated similarly, and more details can be found in Murphy et al. (2017).

Minor comments:

1. ***Line 72: Given the hard ionization in the AMS, there are limits to how much source information can be extracted from AMS data.***

Re: Thanks for the reminding. We have considered the reviewer's comments in the revised manuscript.

Changes in manuscript:

However, given the hard ionization in the AMS, there are limits to how much source information can be extracted from AMS data. Further deconvolution on the contributions of different sources to OA production is challenging.

2. ***Line 82: I don't think that's right. Material in volatility bins is moved as opposed to moving the bins themselves.***

Re: Thanks. We have rephrased the sentence as the reviewer recommended.

3. ***Line 83: It should be made clear that VBS is a framework to represent OA, i.e., the implementation of a VBS does not improve model performance. As the authors already know, it's how the VBS is configured and parameterized is what makes it useful and powerful.***

Re: Thanks. We agree with the reviewer's comments. Each study has improved the configuration and parameters of VBS in the model. We have re-written this sentence in the revised manuscript as follows.

Changes in manuscript:

Previous studies have successively configured the VBS scheme from one-dimensional (1-D) to 1.5-/2-dimensions (1.5-/2-D), which can better describe the evolution of OA in the 2-D space of oxidation and volatility in the model, and coupled the simplified emission inventory of SOA precursors estimated from POA to improve the model performance on SOA simulation (Tsimpidi et al., 2010; Koo et al., 2014; woody et al., 2016; Zhao et al., 2016a; Yang et al., 2019).

4. ***Line 110: ‘catching’?***

Re: Thanks. It has been revised to be ‘reproducing’.

5. ***Line 146: By definition, IVOCs are unlikely to partition to the particle phase at typical environmental conditions.***

Re: Thanks. We have deleted this sentence in the revised manuscript.

6. ***Line 162-163: What is an example of residential solvent use? What was the reason for not including biomass burning?***

Re: Thanks for the reminding. We have deleted this statement in the revised manuscript.

7. ***Line 226: missing ‘and’?***

Re: Thanks. We have added ‘and’ in the revised manuscript.

8. ***Line 311-313: Rephrase SO2 sentence.***

Re: Thanks. We have rephrased this sentence in the revised manuscript as follows.

Changes in manuscript:

The simulated SO_2 was slightly overestimated, which might be caused by the overestimation of SO_2 emissions due to the fact that China's SO_2 emission reduction was far beyond the expectation.

9. ***Line 313: ‘In contrast’?***

Re: Thanks. It has been revised.

10. ***Section 3.1.1: What would be useful is for the authors to discuss why the IVOC-to-VOC ratios are different between sources.***

Re: Thanks for the comments. We have modified the statement in 10. Section 3.1.1 as follows. More detailed discussion may require subsequent experimental studies.

Changes in manuscript:

The chemical materials and production process of these industries were quite different, which would make their G-ratios quite different in the profiles.

11. ***Line 376-379: Lu et al. (ACP, 2018) claim that IVOCs from mobile sources are dominated by cyclic and branched alkanes so I take objection with this statement about aromatics being important (I do find it odd that Lu et al. (ACP, 2020) allot half of the IVOC range emissions to aromatics). More clarification is needed.***

Re: Thanks for the comment. It is really hard to say that the aromatics are dominant in the IVOCs emissions from vehicles, so we have modified this sentence in the revised manuscript as follows.

Changes in manuscript:

Note that IVOC emissions from vehicles included a certain fraction of aromatics, which have faster OH reaction rates and higher SOA yields compared to aliphatics in the same volatility bin (Zhao et al., 2016b; Drozd et al., 2019)

12. ***Table S1: Are the IVOCP4-6 the same as the IVOCP4-6-ALK in Lu et al. (ACP, 2020)?***

Re: Sorry for the mistake. The IVOCP4-6 fractions are also referenced from SPECIATE 5.1 (although the fractions in the database should be derived from Lu et al. and coworkers). We have revised the references in Table S1.

13. ***Lines 448-455: The IVOC model comparison with observations is less than impressive. The model is higher in the summer (9 versus 6.8) and the model is lower in the winter (12.4 versus 18.2). Discussing if this is an emissions or chemistry (or both?) issue would be helpful.***

Re: Thanks for the comment. We have added some discussion in the revised manuscript as follows.

Changes in manuscript:

The modeled IVOCs was higher in summer while lower in winter, not to mention the diurnal patterns and spatial distributions also remained unknown. This may be due to the difference in monthly profiles of I/SVOC emissions, which has not been considered in this study. Another important reason should be the chemical mechanism of IVOCs to SOA evolution still needs to be improved. Continuous long-term measurements of I/SVOC at multiple locations are strongly recommended in the future to help to improve the SOA model performance.

14. ***Line 471: Effect of stronger photochemistry in the summer?***

Re: Thanks for the reviewer's reminding. We have modified this sentence in the revised manuscript.

15. ***Figure S3: Why are there so few OC measurements to compare against? Or have these been averaged for the entire season? Is the model able to capture intra-season variability at each of the sites?***

Re: Due to limited access to data, we used the average OC concentration of the whole season for comparison. We used the observation data from Shanghai Supersite to compare the intra-season variations in this study. In the future, we will try to make more fully comparisons on the daily or hourly variations of other sites with more sufficient data.

16. ***Figure 7: It needs to be made clear how the modeled species representing OA as well as the different AMS factors are aggregated to perform comparisons for 'POA' and 'SOA'. My sense is that there are uncertainties in this aggregation and it is not self-evident that the AMS gets you clean POA and SOA data to compare model predictions against.***

Re: Thanks. We agree with the reviewer that uncertainty exist during the deconvolution of the factors by AMS-PMF analysis. To support factor separations and interpretations, in our current study as well as in two of our companion studies (Huang et al., 2021; Zeng et al., 2022), multiple high time-resolution mass spectrometric techniques were applied and multiple source apportionment methods, i.e., AMS-PMF, Molecular-Marker-PMF, Integrated-PMF were compared to improve the separation and accuracy of the factors. For example, the collocating measurements of primary and secondary organic tracers from cooking (i.e., oleic acid, azelaic acid) sources enable us to further separate an oxygenated cooking organic aerosol factor (OCOA) from the original "lumped" COA factor, yielding a narrowed range for the contributions from COA (Huang et al., 2021). Similarly, an oxygenated hydrocarbon‑like organic aerosol (OHOA) was also resolved based on the measurements of vehicular related organic tracers (i.e., alkanes and hopanes). The oxygenated factors were thus aggregated into the SOA, which originally might be counted as POA in traditional AMS-PMF analysis. Our comprehensive measurements on OA components provide the up-to-date most adequate deconvolution of POA and SOA factors from the perspective of field measurements. To make it clear to the readers, we have revised in the manuscript as follows.

Changes in manuscript:

To further validate the model performance, we compared the simulation results of POA and SOA with those resolved through PMF analysis of organic mass spectral data acquired by an AMS at the SAES supersite. Note that uncertainty exist when directly compare the modeled OA factors with those resolved by AMS-PMF analysis since a clear split of POA and SOA from a measurement point of view can hardly be achieved. To minimize the uncertainty associated with the PMF analysis, comprehensive molecular identification of OA components was conducted and multiple source apportionment model results were compared following the method in Huang et al. (2021a) to improve the accuracy of the factor separation.