Geoscientific Model Development Discussions

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Response to Referee #1

Stella E. I. Manavi and Spyros N. Pandis

Author comment on "A lumped species approach for the simulation of secondary organic aerosol production from intermediate-volatility organic compounds (IVOCs): application to road transport in PMCAMx-iv (v1.0)" by Stella E. I. Manavi and Spyros N. Pandis, Geosci. Model Dev. Discuss., https://doi.org/10.5194/gmd-2022-90-AC1, 2022

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1. T*his study presents a new model to represent the IVOC emissions and SOA formation from on-road gasoline and diesel vehicles in Europe. A SAPRC-based model using 7 new surrogate species was developed based on experimental emissions and smog chamber data. This study shows that IVOC emissions have previously been underestimated by a factor of 8, and the new model surrogates have higher SOA yields than existing VOC model surrogates. The paper does a good job of describing how the new model was developed, but I have a few general questions about the Introduction and Conclusion, and recommendations for how to reorganize some of the information.*

We appreciate the positive assessment of our work by the referee. Following the recommendations of the reviewer, we have revised the paper (including the Introduction, the Conclusion and the SI) to provide additional information about the new model, its parameters and required emissions. These changes are described below (in regular font) following each comment of the reviewer (in italics).

Specific Comments

2. *In this paper you focus specifically on IVOCs. Can you please add a statement in the Introduction stating why you do not investigate SVOCs, LVOCs, or ELVOCs? In Section 2.2 (line 104), you state that the existing PMCAMx VBS model includes volatility bins reaching to 0.01 μg m^{-3}, so it would be good to specifically (briefly) address those compounds as well. I believe lower-volatility species simply were not included in the Zhao work that your model is parameterized on?*

This is a good point. In our previous work during the last 15 years, the VOCs were simulated as independent or lumped species in the corresponding gas-phase chemistry mechanism (SAPRC in our case) and their chemistry was described in some detail. The remaining organics were simulated using the Volatility Basis Set framework following only their volatility distribution and their chemistry was oversimplified. In this work, we take advantage of the developments during the last decade to perform the next step and to add the IVOCs to the species that are simulated with some detail. Unfortunately, it is still too early to simulate the SVOCs and LVOCs explicitly (as lumped species) due to the lack of the necessary information. Hopefully, this will become possible in the near future. We

have followed the advice of the reviewer and added this information in the Introduction.

3. *Line 26-28: Emitted/primary IVOCs also include oxygenated compounds, although these tend to not be emitted from vehicles.*

Indeed, oxidized compounds in the IVOC range, such as phenols and substituted phenols, have been identified in the emissions of biomass burning. As the reviewer points out oxidized IVOCs have not been detected in neither the emissions of on-road vehicles nor in the emissions of other diesel or gasoline powered engines. Additional IVOC species will be needed as our approach is extended to other sources, but the framework is flexible enough to accommodate them easily. This point is now discussed in the corresponding section of the revised paper.

4. *Line 44: "due to their size and low volatility".*

We have made the suggested change.

5. *Lines 63-79: Please give more description why the models described here, which use the same experimental dataset, are insufficient. For example, the model from Lu et al., 2020 already separates the IVOC emissions by C*, kOH, MW, SOA yield, and structure (alkane vs. aromatic). Your model further separates IVOCs into more specific structural categories, which is a difference worth explicitly mentioning in this paragraph and the Conclusion.*

We have followed the suggestion of the reviewer and revised the introduction (lines 63-79) to include a more detailed description of the model developed by Lu et al. (2020). We have also included a description of the differences between our model and the model of Lu et al. (2020) in the Conclusions section, as indicated by the reviewer. The model of Lu et al. (2020), like our model, treats IVOCs as lumped species and it, also like our model, utilizes the work of Zhao et al. (2015; 2016). However, in our model we have chosen to expand on the idea of Lu et al. (2020), by separating the 79 compounds identified by Zhao et al. (2015; 2016) into lumped species based on more specific categories depending on the structure of the molecules and their chemical reactivity. These new lumped species are easily added to the SAPRC gas-phase chemistry mechanism, because they are consistent with its overall structure and philosophy. It should also be noted that the yields and the reaction rate constants with the hydroxyl radical of the new lumped species differ in the two approaches models. We should also point out that we do not consider the Lu et al. (2020) approach to be any means insufficient.

6. *Table 1 is very detailed and may be more appropriate for the SI. Table 1 could instead just give the properties of the 7 new surrogates used in the model (C*, kOH, MW, SOA yields/a_i).*

Table 1 presents detailed information about the individual compounds lumped into each one of the new IVOC species. Despite its length, we would prefer to keep it in the main paper because it will help link the individual species with the lumped compounds in the proposed mechanism. Information about the estimated SOA yields is now provided in

Table 3.

7. *Reference Table 1 (or Table S1, if you move it to the SI) in the second paragraph of Section 2.3 to introduce your descriptions beginning in line 122.*

This is a good suggestion. We have made the appropriate changes and now reference Table 1 before introducing a detailed description of the individual compounds lumped in the new IVOC species in the second paragraph of Section 2.3.

8. *Line 175-177: This is somewhat vague. State explicitly here what the "more volatile products of the reactions" are or state what the "larger lumped VOCs that are already present in the SAPRC mechanism" are. This may warrant an extra table in the SI matching up existing surrogate products with the new surrogate products, or reference the code provided in the Data Availability section.*

We now clarify at this point that the "more volatile products" are the gas-phase oxidation products of the various IVOCs such as peroxy radicals, ketones, aldehydes, glyoxal and others, whereas the "larger lumped VOCs" refer to ALK5 and ARO2. Moreover, as suggested by the reviewer, we have introduced a new table in the SI that provides the composition of the already existing nine anthropogenic and two biogenic lumped species in the SAPRC mechanism.

9. *Lines 182 and 194: Are the OCGi species the same as the 5 products that you reference in lines 173-174?*

Yes, the term OCG_i refers to the five lower volatility products that can partition to the aerosol phase forming SOA. All seven oxidation reactions of the new lumped species contribute to the formation to the same five secondary products in the model. This is now clarified in the revised paper.

10. *Lines 189 and 198: The reactions of ALK7-ALK9 and PAH1-PAH2 should be given somewhere (an in-text or SI table, or referenced to the code provided in the Data Availability section).*

The reactions of the other lumped species are included in a new table in the SI in the revised manuscript.

11. *I recommend reorganizing Sections 2.4.1-2.4.3 and 2.5. Presenting the information more chronologically could be helpful. Reference Section 2.5 in the two sentences in lines 206-209.*

We have changed the order of presentation of the corresponding sections and also reorganized the material in them. We first describe the emissions, then the measurement data, the algorithm used for the fitting and finally the resulting SOA-iv yields. We do connect now the material in the yields section with that of the emissions section.

12. *Line 300 and Figure 1: Are the spatial and temporal distribution of the IVOC emissions determined by the GEMS inventory given in line 292? The spatial and temporal distribution warrant more description since you present the maps in Figure 1.*

Indeed, the spatial and temporal distributions of the IVOC emissions are based on the GEMS inventory. This is necessary because the new IVOC emissions are calculated based on the total VOC emissions from on-road diesel and gasoline vehicles. We have made the necessary changes in Section 3.1 to describe in more detail the temporal and spatial distributions of n-dodecane emissions from on-road diesel and gasoline vehicles over Europe. We also include now in the revised SI a figure with the temporal distribution of the n-dodecane emissions over Paris for a month.

13. *Consider adding figures to the SI for all new surrogates which match the information given in Figures 2 and 3.*

We have followed the suggestion of the reviewer and now include five new figures in the SI that depict the estimated total gasoline and diesel emissions of the compounds lumped into ALK7-ALK9, ARO3 and PAH2.

14. *Line 353: "Estimated based on experimental data and the fitting algorithm".*

We have revised the corresponding sentence.

15. *Lines 355-356: These yields do not match the values given in Table S3. Are these values from the fitted line?*

We now clarify that the yields discussed here are the total SOA yields at a specific concentration and not the yields of the individual VBS species. So indeed, these values are from the fitted line (total yield) and not from Table S3 (yields of individual VBS species).

16. *Lines 408-409: Add reference to the last statement.*

We have added a reference about the differences of the SOA yields of aromatic compounds under high and low NO_x conditions.

17. *Lines 413-414: A benefit of your model is that it matches the same surrogate+reaction scheme of the existing SAPRC model, so it could be easily integrated into existing SAPRC models rather than integrating an entirely new VBS or other model. I think this benefit should be more explicitly stated in the Conclusion.*

We have followed the suggestion of the reviewer and we now highlight this benefit in the revised Conclusions section.

18. *Can you provide a quantitative estimate of how much this model could increase predicted SOA mass in Europe? In lines 427-230 you state that a subsequent study will apply the model, but using the results in this paper you can predict a bulk percent increase of SOA mass over Europe.*

The increase in predicted SOA obviously depends on the simulated conditions. Based on a simple calculation taking into account the new yields and emissions we estimate that the increase would be of the order of 50% for the IVOCs emitted from on-road diesel and gasoline vehicles compared to the default VBS approach currently used in PMCAMx. However, because this is a rough estimate with numerous assumptions, we would prefer to present it in detail in the forthcoming publication.

Technical Corrections

19. *All: Some of the in-text citations use et al. and others use et al*

We have corrected all the in-text citations to the appropriate "et al.".

20. *Lines 89-90: Replace "on" with "to" to avoid the repetition of "on on-road": "In this work, the proposed IVOC scheme is applied to on-road transportation and more specifically to IVOCs emitted by diesel and gasoline vehicles following the studies of Zhao et al. (2015; 2016)."*

We have replaced the preposition from "on" to "to".

21. *Line 93: Name the version of SAPRC, e.g. SAPRC07 or SAPRC99.*

In the current version of PMCAMx, we are utilizing a modified version of SAPRC99. This is now mentioned in the text.

22. *Line 166: "below"*

We have corrected the typo.

23. *Line 201: Be consistent with the tense used. "includes" should be "included".*

Since the whole paragraph is written in the present tense, we have corrected the tense in the following sentence from "was used" to "is used".

24. *Line 296: Define the EUCAARI acronym and give a reference.*

The definition of the acronym EUCAARI (European Aerosol Cloud Climate and Air Quality Interactions project) has been added.

25. *Figure 4: Rename x-axis label "Old" to "Old VBS" for clarity and consistency with the text.*

We have renamed the x-axis label of the figure to improve consistency.

26. *Figure 7: ai (subscript)*

We have corrected the typo.

27. *Figure 10: Add legends.*

We have added the appropriate legends to the figure.

28. *Lines 415-416: "…compared to the IVOC emissions previously used, which assumed that they were equal to…"*

We have corrected the syntax error appearing in lines 415-416.

29. *Line 417: "15%"*

We have corrected the typo.

30. *Line 418: You use MS/GC without defining the acronym, but in line 32 you use gas-chromatograms.*

We have defined the MS/GC (mass-spectrometry / gas-chromatography) acronym.

31. *In the Zenodo link, correct "were" to "where" in the description and correct the title.*

The appropriate changes were made to the Zenodo link.