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Response to Referee #2

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-AC2>, 2022

1. *The paper by Manavi and Pandis presents an interesting framework for a lumped oxidation scheme of IVOC (intermediate volatility organic compounds) compounds and subsequent SOA formation. The scheme relies on a review of recent laboratory studies giving SOA yields for oxidation of parent IVOCs. Such a scheme could be implemented into CTMs for better predicting SOA build-up from IVOC emissions. It shows that IVOC emissions lead to much higher SOA yields as from the highest class of alkane and aromatic compounds in the SPARC chemical mechanism. IVOC emissions from the road sector are also evaluated over Europe. The paper should be of interest for the GMD readership and is recommended for publication after several issues have been addressed.*

We do appreciate the positive assessment of our manuscript. We have made several changes to the revised text (including the introduction, conclusions and methods sections) to improve it and to make the description of our approach clearer. These changes are described below (in regular font) following each comment of the reviewer (in italics).

General comments

2. *The paper is somewhat in between a presentation of a general IVOC oxidation framework and an implementation into PMCAMx, for the case of traffic emissions. As such a case study is reserved for a follow-up paper (this seems acceptable), I suggest to present the development as a general one, being applicable to CTM's in general. Then there is no need to explore the case study and May 2008 European IVOC emissions. For instance, the emission section 2.5 is clearly engaged in explaining how emission data for the European wide case study are built (however lacking details, see my remark below). I would take a step back, and focus on what is provided by the new IVOC module, how these data can be specific for US, as you already say, and what data is needed to couple this with classical emission data.*

We have revised the presentation of our work, where appropriate, so that it refers in general to CTMs and not only to PMCAMx. We do prefer to keep the presentation of the emissions for Europe, both as an illustration of the approach and also as a way to show the magnitude of changes that this new framework brings to the CTM inputs and therefore indirectly show its potential importance. We have also added a short discussion, as

suggested by the reviewer, about the data needed for the coupling of our framework with classical emission data.

3. *My other concern is the benchmark against which the new scheme is evaluated. The proposed benchmark here for yields are the SPARC ALK5 and ARO2 classes for heaviest or heavier alkane and aromatic VOC's. Doesn't this approach mean that you compare to the new model formulation to a model without implementation of IVOC related SOA formation. I would have expected an evaluation against the Robinson et al. (2007) VBS IVOC scheme, which albeit simple, has been probably implemented in many CTMs using the VBS approach. Sure, reference to this scheme is made a many places in the paper, but a comprehensive and quantitative evaluation of differences is not made, and would be an interesting add-up of the study. This could be done in a 0D mode, for example, but not necessarily, starting from average European May 2008 conditions. This would allow discussing how the interplay between higher IVOC emissions, lower kOH rate constants and higher SOA yields in the new scheme presented here affects SOA yields with respect to the former Robinson scheme and also to a scheme without IVOC emissions.*

We do agree with the main point of the reviewer, that the proposed scheme should be compared against the VBS scheme of Robinson et al. (2007). This is actually done for the emissions (see for example Figures 4-6) in the current papers. The comparison for the yields is challenging because the Robinson et al. (2007) scheme produces SOA through a series of aging reactions shifting the volatility of each product generation by one order of magnitude for each generation of reactions. While this original VBS scheme can form significant amounts of SOA-iv, it does it rather slowly and therefore the SOA-iv levels predicted are also affected by the considerable dilution that takes place in similar timescales as the reactions. For this reason, the comparison of the results of the two schemes should be performed in a 3D model, so that one can avoid potential pitfalls due to the oversimplification of important processes. This comparison is performed in detail in the forthcoming manuscript. We have made the necessary changes to the revised manuscript to clarify that the original VBS is an appropriate benchmark for the new approach. We also clarify that we do not use the ALK5 and ARO2 species as benchmarks. We compare the corresponding yields mainly to better connect the new IVOCs with the existing VOCs in the model. These comparisons also allow us emphasize the fact that although the IVOCs have lower emissions than VOCs, their higher yields suggest that they can be important SOA precursors.

4. *Another fundamental difference between the ancient Robinson and the new scheme is that the Robinson scheme only moves mass to next lower volatility class while in the new scheme products can have a large range of volatility. A question : once these IVOC oxidation products formed , do they still further age and subsequently pass to lower volatility classes, as in the initial Robinson scheme ?*

This a good point that needs clarification. In the proposed scheme, the oxidation products of IVOCs do not undergo any further aging once they are formed. However, because we recognize that such reactions may be important, these multigenerational aging reactions have been included in the PMCAMx-iv (v1.0) code but with their rate constants set equal to zero. This is now explained in the revised paper.

5. *Following the philosophy of a new module that could be implemented in diverse CTM models, it would be interesting add a short section indicating the needed model structure*

and input.

Following the recommendation of the reviewer, the revised manuscript includes a short description of the model requirements needed to implement our new lumped species approach.

Specific comments

6. *The paper's title is « 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) ». From this I would expect that the new scheme is run and evaluated at least for a case study, but the paper is restricted to model formulation (which is OK). The scheme can also be implemented to other CTM's quite directly as long as they use the SPARC chemical mechanism. I would suggest to make appear this more general aspect in the paper's title.*

Following the suggestion of the reviewer, we have revised the presentation of our work, where appropriate, so that it refers in general to CTMs and not only to PMCAMx. We understand the point regarding the title of the paper, but given the editorial policy of GMD regarding the model title and version number, the current title is the best solution. We have revised the Conclusions section to emphasize the benefit of integrating our proposed mechanism to models that utilize the SAPRC gas-phase chemical mechanism.

7. *Page 6, line 178: The volatile products of the reactions of the four new lumped alkane species are assumed as a zeroth approximation to be the same as the ones produced by the reaction of ALK5. Even if this may underestimate mass of gaseous products, still this allows to stick as close as possible to existing gas phase chemistry (still some differences due to different OH reactivities). May be worthwhile to say.*

This is a valid point. Indeed, in our approach, the representation of the gas-phase chemistry of IVOCs is significantly improved. We have followed the suggestion of the reviewer and revised the manuscript accordingly.

8. *Page 8, line 215 : the following objective function Q: where $Y_{i,meas}$ are the measured aerosol SOA yields and $Y_{i,pred}$ is the corresponding predicted yield for the choices of the parameters, using the VBS framework. The objective function Q is minimized by using the `fmincon` MATLAB function (MathWorks, 2020). By minimizing the objective function, the optimal ΔH and a_i 's are determined for the chosen C_i^* basis set. » How accurate is this method? The method ideally requires that laboratory results cover the range of OA concentrations from $0.1 \mu\text{g}/\text{m}^3$ to $1000 \mu\text{g}/\text{m}^3$. For some of the compounds in Figure S1, laboratory studies do not cover atmospheric relevant conditions with low enough OA concentrations. Such problems also might have appeared for former studies in the VBS framework, but still the authors should please comment to this question and put some sentences about the limitations of the method.*

We agree with the reviewer that the accuracy of the corresponding yields for atmospheric conditions is determined to a large extent by the availability of the necessary experimental data. The chemical detail of our approach can help here as it can point out to the most important IVOCs for SOA production and thus guide future experimental investigations. This point is discussed briefly in the revised paper.

9. *Page 8, line 230 : « For the individual compounds lumped in ALK7, ALK8, PAH2 and ARO3 there were no experimental data. » I think it should be ALK8 and ALK9 instead of ALK7 and ALK8. A few lines above you say that there are data for ALK7.*

We have corrected the typo in this sentence.

10. *Page 9, line 249: « For example, the mass-based yields of 2,6,10-trimethyltridecane are assumed to be the same as these of n-tridecane. This provides a lower bound for our estimations, as it has been suggested that the SOA yields decrease as the number of branching methyl groups increase ... » Shouldn't it be a higher bound, following your argumentation ?*

This sentence is indeed confusing. We have deleted the last part of the sentence: "as it has been suggested ...increase.". The statement is correct, but it refers to the total number of carbon atoms.

11. *Page 9, section 2.5: In this section, authors describe IVOC emission factors for specific US conditions, which may be a necessary assumption. In Figure 1, they give spatialised emissions distributions for some compounds and for a given month. Authors should indicate the sources of data needed for such estimations (estimations of total VOC and traffic emissions, vehicle fleet partition for the different classes in Table S1, etc.). The simple reference to the former GEMS project is not sufficient. From table S1, it appears that finally only gasoline and diesel cars are distinguished neglecting differences between passenger and light, medium and heavy duty cars. It seems that bulk European fraction of diesel cars is used, but these fractions are different from country to country. May be at the end giving spatialised emission estimates goes to far given the limited data for this study, and this can be left for the follow-up 3D study.*

We have made the appropriate changes to the manuscript and the SI to provide a more detailed description of the method that we utilized to estimate the new IVOC emissions over the European domain. The method does rely on the existence of a spatially distributed inventory for transportation (the GEMS inventory in our case), because it follows its spatial and temporal patterns. Additional information used for the derivation of these spatial and temporal dependencies in GEMS have been added to the paper.