

First of all, we would like to thank the reviewers for their comments. The response to the comments are showed after each comment (in italics).

Anonymous Referee #1

Received and published: 26 March 2018

The Couvidat et al. manuscript reports on a series of parameterizations implemented in a model for secondary organic aerosol (SOA). Model simulation results are compared with experimental data obtained from the Euphore chamber, using both anthropogenic and biogenic precursors. The model used is the SOAP model, which uses surrogate compounds for each precursor that best reproduce the bulk properties of the SOA formed (e.g., O/C and H/C ratios). SOAP model parameterizations are developed for anthropogenic and biogenic precursors, and to represent oligomerization and acid catalyzed uptake of aldehydes. Sensitivity of model simulations to increased particle viscosity and vapor wall loss are considered. While there are some complex processes that are well represented in the model, and these complex processes are treated in a single model framework, the manuscript lacks clear direction. The objectives of the modeling are not clear, nor are the scientific contributions. Development of SOA models has been rapidly advancing over the last 20 years; parameterizations for all of the processes described in this manuscript have been developed and applied. The application of different parameterizations is not particularly novel, nor does it clearly advance the state of the science. It is suggested that this manuscript undergo major revisions prior to publication. The manuscript may be improved by focusing on one of the parameterizations (e.g., oligomerization) and comparing more rigorously to other model parameterizations and a broader suite of published studies. The manuscript should also be read carefully for clarity and grammatical errors. This will also improve the manuscript and increase its potential impact.

We agree that the introduction and the goals need to be clearer. The introduction was rewritten to emphasize the fact that this study is part of an update of the H₂O mechanism using the molecular surrogate approach and that the paper aim at developing (and also evaluating) a SOA mechanism including various processes which are often not taken into account together. We think that only taking into account oligomerization would significantly decrease the interest of the study (and would not have been possible without reformulating the H₂O mechanism). Moreover, our knowledge oligomerization has been scarcely in 3D air quality models as well as the impact of viscosity or the dynamic uptake of aldehyde onto acidic aerosols.

Comments:

The mechanism parameters for aromatics were developed largely from chamber studies that are now 10+ years old. For at least some of the compounds of interest, more recent data are available. For example: Hildebrandt et al., ACP 2015 (toluene) and Li et al., ACP 2016 (aromatics, low NO_x). The same is true of the parameters used to represent oligomerization. See for example, Kundu et al., ACP 2016 (oligomers from limonene). There may be good reasons for using the particular studies/data chosen, but those reasons should be articulated.

This work was initiated a few years ago when the article of Li et al. 2016 was not published and the algorithms are fitted on published Odum's curves data (Hildebrandt et al. do not report any Odum

Curve). Although some of the data used came from old chamber studies, we think that those data are not outdated. As for oligomerization, some parameterizations for 3D modeling were already based on the same experiments of Kalberer. A comparison of the results between these parameterizations is even done in the study. Moreover, no quantitative data are present in Kundu et al. 2012 on the evolution of molar masses with time (that were needed for the development of the model).

Abstract, lines 6-7: replace "were" with "where"

Corrected

p.3, line 20: It is recommended that the authors be more specific about the ranges of conditions covered by the experiments, particularly for atmospherically-relevant conditions that are outside the available datasets.

The range of conditions covered by each of the experiments were summarized in Tables 1 and 2. A sentence is added to refer to these tables, in case this was not enough visible in the text.

p.5, line 3-4: Chamber data studies are referenced twice.

The sentence was reformulated.

p. 7, lines 27-30: How are "short", "big", and "bigger" oligomers defined?

Definitions are added into the text.

Short oligomers: oligomers of 2 to 4 monomers blocks that can be formed quickly during the first hours

Big oligomers: more than 4 blocks of monomers

Bigger oligomers: oligomers with higher molar masses

p. 11, lines 11-15: Can more be said about the underlying reasons for differences between the model simulations in this work with those of Santiago et al. 2012? Particularly from the perspective of describing the likely processes in the experimental studies.

There could be many reasons for the differences between the two studies as the box models used are very different: dynamic approach vs the equilibrium approach, comparison to uncorrected with simulation of depositions to wall vs comparison to corrected values without simulating deposition and how the mechanism in itself was developed or how CMAQ treat the partitioning of secondary organic aerosol. A comparative study would be needed to compare the code of the two models and the data used.

p. 11, lines 31-33: It is suggested that this section be rewritten to clarify that the model simulations are over/under predicting in different chemical regimes. It is not clear as written.

The paragraph was rewritten to improve clarity.

p. 15: The discussion of the consideration of vapor wall loss is incomplete and perhaps misleading. The measurement/model agreement will reflect both the model parameterizations (as indicated), but also the experimental conditions. In this case, underestimation by inclusion of vapor wall loss may largely be due to the fact that vapor wall loss was negligible in the Euphore chamber under the experimental conditions. There is not good scientific support for broadly applying a 3-fold decrease in SVOC volatility and a single vapor wall loss parameterization for all SOA models developed using the

Odum approach as applied to all Teflon chamber studies. The extent of wall loss involves competing kinetic processes, and will be highly dependent on the chamber and the experimental conditions

Due to the uncertainty on the parameter, we initially intended to simply investigate what could be the impact of vapor losses and how it could impact SOA. A value for the vapor loss rate for Euphore is now estimated. Moreover, a mistake producing too much wall deposition was also found and corrected. Section 3.4 as changed.

Anonymous Referee #2 Received and published: 29 March 2018

Couvidat et al. develop updates to a secondary organic aerosol (SOA) model and report their findings on how those updates perform against chamber SOA measurements made with mixtures of biogenic and anthropogenic precursors. They find that, in general, the updates help improve the model-measurement comparison but offer nuanced insights on the role of NO, oligomerization, vapor wall losses, reactive uptake of pinonaldehyde, and particle phase on SOA formation.

The area of study undertaken by the authors is very important, that of understanding the processes that determine the formation, composition, evolution, and properties of SOA from oxidation of organic precursors. Findings here will help develop simplified mechanisms for atmospheric models. However, the manuscript in its current form does not do well in communicating the methods and, in some cases, the results and implications of the modeling efforts (see some comments below for details). What makes the manuscript even harder to understand is that there are numerous grammatical mistakes and phrasing/style issues. These need to be fixed before the manuscript can be reviewed again, in addition to achieving the quality desired in a journal like Atmospheric Chemistry and Physics. Although I believe this is important and novel work, I cannot make a judgement at this point based on the manuscript submitted for review. Hence, I do not recommend publication in ACP until the issues I discuss below are resolved, the presentation quality is significantly improved, and the manuscript is sent out for review again.

Major Comments:

1. Details on experimental methods and data: There is very little description of the experimental methods used to provide context to the modeling in this work. For example, how big is the Euphore facility? Given the size, was it correct to use the same wall loss rate as that used by the Caltech chamber to model vapor wall losses? Was it a Teflon chamber? What was the motivation to use a mix of precursors instead of using a single precursor? Were these photooxidation experiments or ozonolysis experiments (especially for the biogenic mixture)? Was an OH precursor used and if yes, which one? What photochemical ages were achieved? Was ozone produced? If yes, how much? Were these experiments seeded? What instrumentation was used to measure aerosol mass concentrations? How were the data corrected for wall losses? What are the uncertainties in the measurement data? Answers to these questions and more that bear relevance to the modeling need to be provided as part of section 2.1.

Yes, it's true that more information would help to introduce this study. The section 2.1 has been rewritten to provide more information about all these questions.

2. Details on modeling methods: Various details of the modeling approach are missing that make it hard to understand the simulated processes. For example, (page 4, lines 30-32), why was the wall loss

rate for vapors used in this work based on the Caltech chamber. A vapor wall loss rate could be estimated for the Euphore facility based on the calculations laid out in the supporting information of Zhang et al. (PNAS, 2014). Why was this not done? Also, the vapor wall loss rate only defines the loss rate of vapors. The affinity of these compounds to stick to the walls was modeled by Zhang et al. (PNAS, 2014) and later shown by Krechmer et al. (ES&T, 2016) to be a function of the vapor pressure of the species. Was this modeled similarly? In the mechanism section (page 5, lines 1-31), the abbreviations for the different species are obvious but it would be worthwhile to explicitly specify them, e.g., API is never defined. Perhaps, include this information in the tables as a legend. Why is only the number mean used to model particle size and not use the entire aerosol size distribution?

We added more information on the computation of vapor wall losses in section 3.4. Vapor wall losses were calculated similarly to Krechmer et al. and Zhang et al.

Due to the uncertainty on the parameter, we initially intended to simply investigate what could be the impact of vapor losses and how it could impact SOA. A value for the vapor loss rate for Euphore is now estimated. Moreover, a mistake producing too much wall deposition was also found and corrected. Section 3.4 has changed.

The abbreviations are now defined in the text and in the table for the mechanisms.

The following sentence was also added into the text:

“As modeling properly nucleation and coagulation of particles would be needed to simulate adequately the size distribution of particles, particles were gathered inside a single diameter bin.”

3. Structure, grammar, phrasing, and style: In terms of structure, I did not understand the order of the figures. I would recommend that the figure numbers be ordered in the order they show up in the manuscript. Further, the grammar, phrasing and style could be significantly improved. Here is a sample of mistakes I found just in Section 3.3 on page 13: (a) line 8: ‘they dynamic of the uptake’, (b) line 18: ‘specific of the compound’, and (c) line 18-19: ‘probably provides a good estimate and order of magnitude.’. The manuscript is littered with such mistakes.

The order of figures was changed, following the reviewer advices.

Several mistakes and grammar errors were corrected. A spell check by the editors will be asked for to track any remaining mistakes.

Minor comments:

1. Page 2, line 13: Consider citing the chemical transport model study of Cappa et al. (ACP, 2016) that simulated the influence of vapor wall losses on organic aerosol (OA) mass concentrations in urban areas.

Reference added.

2. Page 2, line 14: Jathar et al. (ACP, 2016) have showed – similar to the findings in this work – that oligomerization may not play an important role in affecting SOA mass concentrations but may change the SOA composition. Consider citing.

Reference added.

3. Page 3, line 17: How big is the Euphore facility?

Details were added in section 2.1. The volume of Euphore is 202 m³.

4. Page 4, line 29: *What does chamber is closed mean?*

“closed” replaced by “enclosed by the retractable steel housing.” Explanation are added in section 2.15. Page 5, line 23-29: *Are the different O:Cs possibly from differences in OA mass concentrations in the different experiments?*

The mean O/C may indeed change for different concentrations of OA. However, the precursors and the chemical regimes are probably the most important elements. The range of H/C and O/C from the cited studies are obtained from a variety of conditions with various organic aerosol loading.

6. Page 11, line 7-8: *Is particle number or mass used to determine particle wall loss rates? Why are the particle wall loss rates different for with and without oligomerization?*

In these simulations, the wall deposition rate was constrained to reproduce with the model the decrease of SOA volume concentrations (measured with the SMPS) during the last hours of the experiments. As the computed evolution of SOA concentrations during the last hours can be slightly different with or without oligomerization, the wall deposition rate used with and without oligomerization are different.

7. Page 11, line 28: *Could the differences in SOA formation be explained as a function of the VOC/NO_x ratio expressed in ppbC/ppb, similar to previous work?*

The following sentence was added to justify the use of the chemical regime ratio

The chemical regime ratio was used instead of the VOC/NO_x because in this study a mixture of VOC (and not a single VOC) was present in the chamber. The chemical regime ratio takes into account the reactivity of the compounds and can therefore be used to compare different experiments with different mixtures of VOC.

8. Page 12, line 17: *Use ‘fragmentation’ instead of ‘fractionalization’.*

Corrected

9. Page 14, line 7-8: *Sentence is unclear and needs more explanation.*

“For non-viscous aerosols, deposition of particles to wall can lead to the evaporation of SVOC due to a decrease of the absorbing mass.” Replaced by “For non-viscous, deposition of particles to the walls lead to a decrease of the absorbing mass (mass of the organic aerosol). As the gas/particle partitioning is proportional to the absorbing mass, SVOC will evaporate to maintain the gas/particle partitioning whereas this evaporation will be limited for a viscous aerosol.”

10. Page 14, line 14-15: *What figure shows a factor of 3 difference for the simulation that includes the loss of vapors to the walls.*

Reference to the figure added.

11. Page 14, line 23: *What do stoichiometric coefficients mean here?*

Detail added.