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Atmospheric
Chemistry
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Discussions

# *Interactive comment on* “Explicit modelling of SOA formation from $\vec{\alpha}$-pinene photooxidation: sensitivity to vapour pressure estimation” *by* R. Valorso et al.

**Anonymous Referee #2**

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In this study sensitivity of predicted aerosol mass and aerosol composition towards choice of vapour pressure method is investigated. Three vapour pressure methods were considered. Also comparison with experiment, in the form of smog chamber experiments, is provided. Important information for chemistry modellers is the approach used to reduce fully explicit mechanisms to a tractable size (from a box model perspective), without significant loss of accurracy.

I recommend publication of this paper in ACP, but only after the following issues and questions have been addressed.

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## 1 General comments

### 1.1 Extension the set of vapour pressure methods

The authors have investigated the vapour pressure Myrdal-Yalkowsky (MY), combined with the Joback-Reid boiling point method, the Nannoolal vapour pressure method, combined with the Nannoolal boiling point method, and the SIMPOL method. Three methods is not that much for a sensitivity investigation. From the work of Barley (2010) and Compernolle (2010) one can see that MY combined with Joback-Reid gives relatively low vapour pressures, while the other two are intermediate. The authors should include at least one other method that gives rather high vapour pressures. The easiest way to do this is to include the MY method combined with the boiling point method of Nannoolal (2004), as they have already implemented these methods. This method also came out as second-best in the study of Barley (2010).

### 1.2 More thorough investigation of the reasons for the insensitivity to vapour pressure method.

On page 10133, line 21, the authors state: "Nevertheless, the simulated SOA concentrations show an unexpectedly low sensitivity to the method used to estimate $P^{\mathrm{vap}}$, well below the $P^{\mathrm{vap}}$ variability shown in Sect. 3 for the semi-volatile organic species." but they do not give an explanation.

It could for example be that the different methods predict not very different vapour pressures for the top ten compounds. This is certainly possible, as the hydroperoxy compounds are important contributors to SOA, and the hydroperoxy group contribution is derived for all methods from the same, small set of vapour pressures. Agreement among the different methods would in this case certainly not imply a large reliability of the estimated vapour pressure for these compounds! This should be investigated. In

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case variability of predicted vapour pressure is indeed low among the top contributors, the authors should add a study with one or more methods with an added bias and/or random scatter to the estimated vapour pressures. This bias and scatter can be based on the results in Table 2.

The authors compare the model results for one low, one intermediate and one high NOx experiment. From Fig. 5 it is clear that, both experimentally and by modelling, the aerosol mass produced is the highest for experiment 1 and the smallest for experiment 3. It could be that $\xi_i^{\mathrm{aer}}$ is close to one for the important contributors for experiment 1, while it will be less for experiments 2 and 3, possibly closer to 0.5. Then the increasing variability to vapour pressure method in the order 1-2-3 would not be directly related to the high NOx conditions, but only to the lower aerosol mass. This should be investigated. This also means that for atmospheric simulations, where aerosol mass is low, sensitivity to vapour pressure estimation method will be much important than for smog chamber simulations with typically larger aerosol masses. This should be reflected in the discussion.

Of course, the above considerations also apply to the aerosol composition. The ranking agreement is poorer for the simulations with higher NOx/lower SOA (Fig. S4), than for the low NOx/high SOA simulation (Fig. 7). This could be due to a $\xi_i^{\mathrm{aer}}$ closer to 0.5. This should be reflected in the text. Also introducing a bias and random scatter (see above) could have a significant impact on the aerosol composition.

## 2 Specific comments

p. 10124, line 15. The authors use 'MY' to refer to the Myrdal-Yalkowsky vapour pressure method, which is in their work combined with the Joback-Reid boiling point method. This gives the wrong impression that choice of boiling point method is only of secondary importance. It gives also the strange result that the 'MY' method gives the lowest vapour pressures and highest SOA yields, while it is stated in Barley (2010) that MY 'does have a bias towards overestimating vapour pressures'. Therefore I would recommend a naming that reflects the composite nature of the method, e.g. JR/MY.

p. 10127, line 14-16. This sentence is too vague. How are the criteria used to discriminate? Will at the end of the discrimination process only one isomer remain to represent all other isomers? Is the order of the criteria, as tabulated in Table 1, relevant in this discrimination process? A figure demonstrating the lumping process (e.g. from 5 to 1 molecule) could help here. If the order of the criteria is relevant, have the authors investigated the impact of criteria ordering on the performance of the lumping process (accurracy of the lumped mechanism)?

p. 10127, line 18-21. On which systems was this tested? What is the size of the error induced by the lumping process?

p. 10127, line 24. Peeters and coworkers have provided important updates to the chemical oxidation mechanism of $\alpha$-pinene by OH (Vereecken, 2007) since 2001, regarding the chemistry of one of the peroxy radicals. Why was this not used?

p. 10128, line 1-5. According to quantum chemistry calculations, the described 1,7 H-shift is negligible compared to decomposition (Capouet, 2008). So why is this path used?

p. 10131, line 10-13. The authors state that photolysis constants and wall deposition of semi-volatiles were optimized parameters, and that the optimized parameters are given in Table 3. Yet I cannot find them there!

p. 10131. While the authors mention briefly the wall loss of gases, they do not mention wall loss of aerosol. Was it incorporated in the modelling study? Or was it already corrected for in the experimental data? This should be mentioned.

p. 10132, line 8. What could be the reason for the ozone overestimation? Mechanism uncertainty or a chamber artefact?

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Table 1. Crit. 9. Does 'conjugated carbonyls' only apply to ketones, as '-CO-CO-' seems to suggest? Then 'conjugated ketones' would be a better term, as aldehydes are also carbonyls.

Crit. 13. What is exactly meant by 'conjugated carbonyls at a terminal end of the chain'? Does this also only apply to two ketone functionalities? A ketone cannot, by definition, be at the very end of a chain, then it would be an aldehyde. Are structures like -CO-CO-CH3 meant? Note that also structures such as -C=C-C=O can be called 'conjugated carbonyls', which adds to the confusion.

Crit. 5-8. Are nodes defined in the graph obtained from the hydrogen-suppressed molecule? This should be specified. Surprisingly, there is nothing on double bonds in this set of criteria, while the double bond is definitely important in mechanism construction. Was this investigated (e.g. conjugated double bonds vs. nonconjugated double bond, -C=C-C=O vs. nonconjugated alkenoic carbonyls).

Table 3. Does '-' mean zero? This should be specified. The simulated photolysis frequencies should be included in 'optimized parameters', as well as the wall-loss parameters.

Table 4, and Table S1: add vapour pressures of the top 10 compounds, and their condensed fraction $\xi_i^{\mathrm{aer}}$.

## 3 Technical corrections

Spelling inconsistency: functionalized/functionalised, optimized/optimised, functionalization/isomerisation are both used in the text.

The authors use 'difunctional' for species with two functional groups, while 'bifunctional' is more common.

p. 10122, Eq. (1) is not Raoult's law. It only becomes so after setting $\gamma_i = 1$. Reword.

Table 2. Add vertical space between $n$ 108 1179 . . . and MAD MY-SIM.

Caption of Fig. 9. "As a function of the type of function". This should be "As a function of the type of functionality".

## References

Capouet, M.; Müller, J.-F.; Ceulemans, K.; Compernolle, S.; Vereecken, L. Peeters, J., Modeling aerosol formation in alpha-pinene photooxidation experiments, J. Geophys. Res., 2008, 113, D02308

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Barley, M. H. McFiggans, G. The critical assessment of vapour pressure estimation methods for use in modelling the formation of atmospheric organic aerosol Atmos. Chem. Phys., 2010, 10, 749-767

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