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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Parameterising secondary organic aerosol from $\vec{\alpha}$-pinene using a detailed oxidation and aerosol formation model" *by* K. Ceulemans et al.

Anonymous Referee #2

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This study presents a new parameterized model for simulating secondary organic aerosol formation from a-pinene photoxidation, taking into account the effects of temperature, oxidant, NOx level, water, and aerosol aging. This is an interesting approach as it allows for some descriptions of the detailed chemistry, yet maintains the model at a relatively simple scale which can potentially be used in global SOA modeling.

This paper contains a large number sections and subsections owing to the many different experimental conditions investigated. The paper is generally well-written, however, there are some sections which could be better organized and explained (please see detailed comments below).

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The authors interchanged the use of terms such as “full model”, “fitted model’, “parameterized model”, “box model”, “parameterized BOREAM model”, “BOREAM full model” etc throughout the manuscript. It is confusing at times as to which model the authors are referring to. This makes it difficult to interpret some of their results and follow the discussions. The authors should be consistent in their description and use of different terms, both in the text as well as the figure labels.

I recommend publication in ACP after the comments are addressed.

(For the comments below, I will refer to the full BOREAM simulation as “full model” and the 10-product model as the “parameterized model”)

Specific comments:

1. Many of the sentences in the manuscript contain too many commas thus making the sentences very fragmented and difficult to follow. For example, the last sentence on page 23426 and line 20 onwards on page 23435.

2. Section 2.3: The authors wrote “The present model version includes aerosol phase photolysis, with identical J values and product distributions as in the gas phase, in view of lack of more reliable data”. Does this mean that the authors consider only the photolysis of those species that are present in both particle- and gas-phases? Can this potentially underestimate the effect of photolysis by excluding the photolysis of compounds that are only present in the particle-phase? (formed through particle-phase reactions etc).

3. Page 23434, last paragraph of Section 2.5:

a. Line 3. “Modeled and experimental SOA mass yields. . ..” I assume the authors are referring to the “full model”? The authors should be consistent and clear with their use of different terms such as “full model”, “fitted model’, “parameterized model”, “BOREAM model”, “BOREAM full model” etc.

b. Line 4. The authors noted that the factor of 2 of overestimation may arise from

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uncertainties in yields of products such as pinic acid formed in ozonolysis reactions. However, as a-pinene ozonolysis and photooxidation form very similar products, such products are also formed in a-pinene photooxdation. How does this uncertainty affect the results of their photooxidation simulations?

4. Page 23436. According to the authors, the full model is conducted under 5 scenarios in which a-pinene is limited to one oxidant under high or low NOx conditions. But in the "a-pinene + O3, high NOx", is the a-pinene truly only reacting with ozone? With the presence of NOx, some OH will be formed (I think this is how "traditionally" photooxidation experiments have been carried out in the past, for example, Odum et al, Griffin et al., before the use of H2O2 and HONO). I will expect some a-pinene will react with OH. Hence it's not truly "limited to one oxidant". Please clarify.

5. Page 23438. Comparison of full model and parameterized model, Figure 1. Why does the Mo start at higher values with decreasing temperature? The parameterized model seems to level off at higher Mo values but not the full model, why?

6. Page 23439. Regarding the intermediate NOx experiment, the authors wrote "In the full model, however, a reaction with HO2 can be followed by a reaction with NO, leading the formation of a much volatile product." Why is that such reaction (a reaction with HO2 can be followed by a reaction with NO) only occurs in the full model but not the parameterized model? Shouldn't the branching of RO2+HO2 vs RO2+NO be taken into account in the parameterized model too and hence the RO2 in the parameterized model can also react with NO? (since the authors have obtained different parameters for low NOx and high NOx conditions, I would expect the parameterized model should also be able to handle the intermediate NOx condition).

7. Page 23440. Sensitivity of photolysis as well as OH and HO2 concentrations. In Figure 5 the authors present the results on the effect of NO2 levels on BOTH the full model and the parameterized model. However, in Figure 6, they only present the results on the effect of photolysis/OH/HO2 on the "BOREAM model" (as noted in the

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axis label). Is this (Figure 6) the full model or the parameterized model? If it is the full BOREAM model, then what are the effects of photolysis/OH/HO2 on the parameterized model? Is that similar to the full BOREAM model?

8. Page 23441, line 4. "Small but significant uncertainty?" – what does this mean? Small, or significant?

9. Page 23441. Section 3.5:

a. The title of this section is "Comparison with parameterized models based on experimental yields". I am very confused whether they are comparing the results from their full BOREAM model or parameterized model to other models. In their discussions, it seems like they are referring to the parameterized model. However, in the figure, the results are referred to as "BOREAM" and they look different from those parameterized models results in Figure 3 (for example, in Figure 3, the SOA yield at Mo=30 ug/m3 for OH, low NOx is < 0.5, but in Figure 5, the SOA yield at Mo=30 ug/m3 for OH, low NOx is > 0.5). This section needs to be clarified as to which model they are actually discussing about.

b. Figure 1 and Figure 6 both compare the results from this study to other studies. The manuscript will be more well-organized if the descriptions of these two figures were combined and discussed in a more-coherent way. If possible, the authors should also put other data points (instead of just Ng 2007) on Figure 6. Note: Two data points (black *) in Figure 6 are labeled as Ng 2007 high-NOx. One of those experiments should be an intermediate NOx experiment instead of high-NOx (I think probably that is why the authors excluded that in Table 2). This needs to be corrected.

c. The authors noted that one of the reasons for the large difference in the simulated yields and measured yields could arise from the shorter duration of the experiments (several hours) as oppose to the multi-day aging in their models. However, as the authors pointed out, Presto et al. high-NOx experiments agreed well with their high-NOx simulations. The experiments in Presto et al. were performed in a 10m3 chamber

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under moderate oxidation conditions; I do not think multi-day aging was achieved in those experiments either. If the authors' argument is correct, how would that explain the good agreement between the Presto et al results and their results?

d. The authors noted that under low-NOx conditions, aging increases their simulated SOA yields through further reactions with OH and HO2, while under high-NOx conditions, aging decreases their simulated SOA yields through decomposition of the products. However, in the high-NOx experiments, shouldn't the prolonged exposure to OH also increase functionalization of some products and lead to a higher SOA yield? Please clarify.

10. Has the effects of aqueous-phase chemistry (e.g., Ervens et al., 2011) been considered in all these simulations?

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 23421, 2011.