

Interactive comment on “The roles of volatile organic compound deposition and oxidation mechanisms in determining secondary organic aerosol production: A global perspective using the UKCA chemistry-climate model (vn8.4)” by Jamie M. Kelly et al.

Anonymous Referee #1

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General Comments

This work expands the SOA description in the United Kingdom Chemistry and Aerosol (UKCA) chemistry-climate model, and adequately explains why there is need for a more complex description of SOA formation in UKCA. The work also compares UKCA against global observations reasonably well. However, major revisions in the design of the model set-up and interpretation of the results are needed. These changes are

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more explicitly stated in the specific comments, but generally described here. With these changes, the work has a potential to make a nice contribution to the field.

-There is no mention of the higher SOA yields for toluene measured in Zhang et al., 2014 paper. This paper determines that when chamber vapor wall loss effects are accounted for, the toluene SOA yields increase significantly for both the RO₂ + NO and RO₂ + HO₂ channels compared to previous studies. The work mostly cites a paper (Ng 2007) from the same group, but 7 years prior. The results in Zhang et al., 2014 paper should be considered in this work and used to form a basis for the sensitivity tests that are performed.

Xuan Zhang, Christopher D. Cappa, Shantanu H. Jathar, Renee C. McVay, Joseph J. Ensberg, Michael J. Kleeman, and John H. Seinfeld: Influence of vapor wall loss in laboratory chambers on yields of secondary organic aerosol, 111 (16), 5802-5807, doi: <https://doi.org/10.1073/pnas.1404727111>, 2015.

-There is a lot of discussion about how in the aromatic system the RO₂ + NO pathway forms semi-volatile compounds and the RO₂ + HO₂ pathway forms non-volatile compounds. This work does not benefit from such a discussion. The SOA gas surrogate species irreversibly forms SOA in the model used in this work in all simulations. The work is misleading to suggest that the difference in volatility is accounted for by increasing the SOA molar yield. To account for volatility a surrogate species that will reversibly partition to the particle-phase based on its volatility is required. Accurately representing this process has different consequences than increasing the SOA yield. More commonly and possibly more applicable to this study, the RO₂ + HO₂ products are seen as more functionalized with a higher SOA yield and RO₂ + NO products are seen as more fragmented with a lower SOA yield.

-Throughout the work, the advances to the SOA scheme are labeled as multigenerational. This is very misleading. Multigenerational typically does not include the peroxy radical as another generation. For example, A + OH → RO₂; RO₂ + NO → Organic

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nitrate. This organic nitrate as the first non-radical stable product, is a first-generation product. If Organic nitrate + OH-> products is added, this is a multigenerational set-up. For consistency, with past work and the general use of multigenerational in the field, I would suggest changing this to RO2 fate throughout this work. Also the work spends a lot of time discussing how adding the RO2 radical step may delay SOA formation and states that the RO2 radical has a lifetime with respect to oxidation of ~ 1 day. This should be verified. For example, a good recommended source for describing RO2 oxidation in the atmosphere, Orlando et al. 2012, suggests at most this RO2 lifetime is many minutes.

John Orlando and Geoffrey Tyndall: Laboratory studies of organic peroxy radical chemistry: an overview with emphasis on recent issues of atmospheric significance, Chemical Society Reviews, 41, 6294-6317, doi: 10.1039/C2CS35166H, 2012.

-Overall and as explained in the specific comments below there is not sufficient justification for why the test cases were chosen.

Specific Comments

-Page 4 line 21: "As aromatic oxidation is initiated by the hydroxy radical, the influence of NOx on SOA production is probably due to reaction of NO with second or later generation oxidation products" -> Please rephrase this, see general comment. The peroxy radical is not a second generation product.

-Page 4 line 23 and Figure 1: "Oxidation of the parent aromatic hydrocarbon . . . forming a bicyclic peroxy radical, RO2" The bicyclic peroxy radical is only the dominant mechanism for OH oxidation of an aromatic compound, there are other pathways too. The Johnson et al. 2004 paper that is cited does not explain the formation of this bicyclic peroxy radical. Johnson et al. 2004 discusses alkane alkoxy radicals. There are many sources to cite here (e.g., Birdsall 2010), who first measured the bicyclic peroxy radical. Birdsall also discusses the full chemistry that occurs for aromatics.

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Adam W. Birdsall, John F. Andreoni, and Matthew J. Elrod: Investigation of the Role of Bicyclic Peroxy Radicals in the Oxidation Mechanism of Toluene, J. Phys. Chem. A., 114, 10655-10663, doi: 10.1021/jp105467e, 2010.

-page 8 line 11: How does condensation aging relate to the previous sentence? Are there additional aging processes in the model? Is there any aging of the SOA?

-page 8 line 27: "into the insoluble mode and transferred into the insoluble" Please clarify/rephrase?

-page 9 line 22: Please clarify this first sentence. What else would produce SOA other than VOCs in the model?

-page 9 section 2.5: Please clarify. Does VOCant/bb only undergo OH oxidation in the default and the updated mechanism? Perhaps, adding this to Table 1 would be useful. Are the VOCant/bb assumptions for reactivity determined in this work or another work? Further description on why these assumptions were made would be useful.

-page 10 line 5: Are the parent hydrocarbons because they are SOA precursors also wet and dry deposited using the high henry's law constants ($> 10^5$)? Parent hydrocarbons like isoprene are well established to have lower henry's law constants. Is there only one tracer for SOG?

-page 10 line 9: Why use a henry's law constant range for wet deposition and not also test the same range for dry deposition? This seems like a more consistent approach and more fairly capturing the actual uncertainties. Using the experimentally observed surface resistances does seem reasonable for the ROOH as SOA precursors are likely to have hydroperoxy groups. However, why bound the uncertainty with CO? Are SOA precursors expected to act similarly to CO? This likely adds extra unnecessary uncertainty to the model results.

Page 11 line 13: See general comment above. It is misleading to suggest that increasing the SOA molar yield will account for the difference in volatility between different

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products. To account for volatility differences in a model you must have SOA precursors that are able to reversibly partition to the particle phase.

Page 12 line 18: "RO₂ and SOG have differing relative molecular masses. Consequently, a stoichiometric yield of 66% corresponds to a mass yield of 100%. Therefore, 66% is the highest stoichiometric yield that ensures conservation of mass without the addition of other atoms, such as oxygen" Please clarify. The logic here seems incorrect. First, why choose the highest SOA yield possible? Why not use an SOA yield measured/constrained from experimental studies (e.g., the SOA yields measured by Zhang et al., 2014)? Second, why is mass conservation necessary. Although this reaction is written as one step it is really a parameterization of many reactions and so does not need to follow the laws of mass conservation. Although very unlikely, the highest SOA yield possible is unity molar yield from the parent VOC molecule. The same example I used above. $A + OH \rightarrow R$; $R + O_2 \rightarrow RO_2$; $RO_2 + NO \rightarrow$ Organic nitrate. This organic nitrate has a lot more mass than the parent molecule A, because it is more functionalized and has gained oxygen and nitrogen atoms by reacting with OH, O₂, and NO.

-Page 13 line 22: Were the model and observations compared separately in 2000, so that there would be comparisons over the same year the model was run? How do these 2000 results compare to the 2000-2010 more general results? From 2000-2010 there are substantial changes in anthropogenic and fire emissions, which would make it difficult to interpret these results.

Figure 4 and Figure 13: What is the averaging for the model and observations used to get these points? Was any seasonal analysis conducted? Are these points a mix of different seasons?

-Page 14: Please add some explanation in the paragraphs below or elsewhere in the paper about how this work might differ between past work. Not necessarily in overall magnitudes, but in approach. For example, this work uses SOA precursors that

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irreversibly form SOA, while past work has used SOA precursors that reversibly form SOA (e.g., volatility basis set). Explain how this might affect the results in this work especially the impact of wet/dry deposition?

-Section 5: This section would be much more effective if it were written more concisely.

-Page 19 line 12: See general comment above. The use of multigenerational here and throughout the work is misleading. I would suggest phrasing this instead as RO₂ fate.

-Page 20 line 18: The lifetime of the RO₂ radical being ~1day is quite unexpected. Please confirm this and considering the actual RO₂ radical lifetime, rephrase this section.

-Page 21 line 6: Is NO actually high in the Amazon in your model? It looks low in Figure 11.

-Page 23 line 14: Increasing the molar SOA yield is not equivalent to changes in volatility. Please rephrase this and all paragraphs in this discussion. Unless you change the volatility of the SOA precursors and have SOA form reversibly you are not actually accounting for the changes in volatility.

-Page 23 line 16: See above, please reconsider/clarify why 0.66 was chosen as the SOA molar yield?

-Page 29 line 27: Please expand on this paragraph.

-Table 2: Please explain how the field studies were used to derive these surface resistance values. What would these surface resistances be, if the Henry's law constants used for wet deposition were used here instead?

Technical Corrections

-NO_x sometimes has x subscripted and sometimes not. -You have 2 section 2.5 - There are a number of spelling errors throughout as noted below: -page 2, line 4 (improvements), line 6 (observations) -page 6, line 13 (precursors) -page 15, line 33

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(respectively) -page 18 line 12 (translated) -page 26 line 26 (respectively) -page 26 line 28 (chemistry) -page 27 line 3 (Africa)

Interactive comment on Geosci. Model Dev. Discuss., <https://doi.org/10.5194/gmd-2018-142>, 2018.