

Interactive comment on “Differences in BVOC oxidation and SOA formation above and below the forest canopy” by Benjamin C. Schulze et al.

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We thank both reviewers for their insightful comments regarding the manuscript. Many of the issues addressed had a substantial impact on the modeling framework and subsequently the results. These are described in detail below.

REVIEWER #2

1. Referee:

The authors dedicate lengthy discussions to obvious and/or unsurprising results. Some examples include: (1) that isoprene oxidation is predominantly by reaction with OH is mentioned in the abstract and has a dedicated paragraph (p. 11, lines 23-29) and figure (Figure 6); (2) an entire section is dedicated to detailing the enhancement in daytime

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nitrate concentrations (Section 3.2, p. 10), but this can be reduced to 1-2 sentences pointing to the importance of photolysis; and (3) page 8, lines 30-34: that NO₃ and O₃ perturbations change NO₃ is obvious and indicated in Equation (4).

Author Response:

We agree that shortening or removing these specific cases (which were included for completeness and proof of model performance) is an appropriate change. With regard to the section describing NO₃ concentrations, because NO₃ is sensitive to both photolysis rates and O₃ and NO_x profiles, which are substantially different above and below the canopy, we considered it appropriate to include a short analysis highlighting the specific times when reductions in photolysis caused the elevation in NO₃ concentrations, rather than simply claim that this was the case during the middle of the day.

Resulting changes in manuscript:

The revised manuscript will show that: - The mention of isoprene oxidation has been removed from the abstract, as has most of the original paragraph describing isoprene oxidation. Only one sentence has been included at the end of the previous paragraph. - The section describing the daytime enhancement in NO₃ concentrations below the canopy has been reduced and added to the section regarding NO₃ concentrations. - The section describing the NO₃ steady state analysis has been removed.

2. Referee:

Steps in the methodology are not well justified and so appear arbitrary. For example, the authors include observations from a site in Detroit and also appear to impose an imaginary forest canopy in the 0D simulations. The analysis of the CABINEX site under polluted conditions seems sufficient to show the effect of pollution on RONO₂ and SOA formation above and below a forest canopy.

Author Response:

Please see response to Reviewer #1, Point #6.

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3. Referee:

It is not clear from the abstract or concluding statements what the impact is of the results from this study. Are there any implications in this study for greening urban areas or for rapid urbanization (that is, rapid land cover change in and around urban areas)? In the Short Summary the authors mention that it is important to understand the impact of forest canopies on the oxidative fate and SOA formation of reactive VOCs “as forested areas downwind of urban areas (and therefore the residents) will be impacted by this phenomenon.” How will they be impacted?

Author Response:

We acknowledge that a discussion of impacts of the study could be expanded. Ultimately, we conclude that the elevation of NO₃ below the canopy influences organic nitrate production rates substantially during the day, leading to a different suite of organic nitrate products above and below the canopy. The effect of elevated NO₃ concentrations on SOA formation becomes more significant under polluted conditions with a favorable NO₂/NO ratio, which could indicate that forested areas on the outskirts of urban environments may experience substantially higher SOA mass loadings below the canopy than above the canopy, potentially affecting the health of local communities.

Resulting changes in manuscript:

Both the abstract and the conclusions in the updated manuscript will make the implications of the results more explicit.

SPECIFIC COMMENTS, REVIEWER #2

4. Referee:

Page 2, line 2: The start of the sentence “The most significant first-generation RONO₂ formation mechanism” is ambiguous. Do the authors mean that most RONO₂ is first-generation RONO₂ or is this referring to a specific first-generation RONO₂ species that dominates?

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Author Response/Changes in Manuscript:

Because of the large number of changes incorporated into the model based on both reviewers' suggestions, especially with regard to the sensitivity analysis, this sentence will no longer be relevant.

5. Referee:

Page 2, lines 28-29: Will the 0D model in this study then also underestimate OA mass loadings?

Author Response/Changes in Manuscript:

Our model may underestimate OA mass loadings, as understanding of oxidation, partitioning, and particle-phase chemical mechanisms (oligomerization, the effect of liquid water) are not yet complete enough to ensure entirely accurate results. The aim here is to highlight the potential importance of NO₃ chemistry. However, the inclusion of recently discovered pathways for SOA formation (ELVOC formation and reactive uptake of isoprene products) reduces the amount of under-prediction. Furthermore, by ensuring that we under-predict rather than over-predict SOA mass loadings, we can be confident that our conclusions are conservative with respect to SOA formation. These points will be emphasized in the description of limitations of the SOA modeling in the updated manuscript.

6. Referee:

Page 3, lines 20-21: Are the authors referring to a previous study when they state: “It has been further hypothesized that”? If so, then please provide the reference.

Author Response/Changes in Manuscript:

The mentioned sentence has been altered to read, “Furthermore, the majority of these studies have modeled relatively remote locations, encouraging an evaluation of the sensitivity of modeled results to background pollutant concentrations.”

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7. Referee:

Page 3, line 37: Please briefly indicate for the reader what the differences are in BVOC (isoprene and alpha-pinene) reactivity and SOA formation.

Author Response/Changes in Manuscript:

The following sentences have been added to the manuscript at the appropriate location:

“For instance, isoprene is known to react predominately with OH, while α -pinene reacts substantially with all three major oxidants (Fuentes et al., 2006). The SOA yields measured during the photooxidation of isoprene are generally lower than those from α -pinene (0-0.053 for isoprene; 0.06-0.21 for α -pinene); however, their SOA yields are similar under conditions of NO₃ oxidation (0.04-0.238 for isoprene and 0.04-0.16 for α -pinene) (Spittler et al., 2006; Ng et al., 2007; Carlton et al., 2009). As α -pinene is much more likely to react with NO₃ than isoprene, this study highlights potential differences that increased concentrations of NO₃ can have on SOA formation from different VOCs.”

8. Referee:

Page 4, lines 21-24: Please indicate what the effect is of not accounting for liquid water content and particle-phase reactions on SOA predicted by the model.

Author Response/Changes in Manuscript:

The following sentences have been added to the updated manuscript.

“As these particle-phase reactions can rapidly produce high MW, low volatility compounds, often more aerosol mass is produced in the environment than equilibrium partitioning of the gas-phase species would predict (Johnson et al., 2005; Kroll and Seinfeld, 2008). Furthermore, as increases in RH, and subsequent increases in the water content of SOA, are known to enhance the partitioning of organic species to the aerosol phase, the omission of this process also potentially leads to underestimation

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of the total amount of SOA formed (Hennigan et al., 2008). However, as aerosol liquid water is generally driven by inorganic aerosol components (Carlton and Turpin, 2013), which only comprised a small fraction of total aerosol mass during CABINEX, the overall effect of RH is predicted to be small for the conditions of this study (Malm and Day, 2001; Hennigan et al., 2008; VanReken et al., 2015). Therefore, the primary uncertainty in aerosol formation is related to the production of high MW compounds through particle-phase reactions, but these compounds are partially accounted for through the parameterization of ELVOC formation.”

9. Referee:

Page 6, line 1: “...varies over the range of 0 to 0.17.” This range includes night time, but more useful for the reader is the variability in this ratio during daylight hours when photolysis is occurring.

Author Response/Changes in Manuscript:

The above has been changed to “. . .varies over the range of 0.05 to 0.17 during daylight hours.”

10. Referee:

Page 6, lines 1-2: “Model input data are further described in the SI”. There is no description of the model input data in the SI; only figures and captions.

Author Response/Changes in Manuscript:

The above has been changed to, “Model input data are shown in the figures in the SI.”

11. Referee:

Page 6, line 13: “In the second modeled case...”. What was the first modeled case? This is not systematically presented in the methods section.

Author Response/Changes in Manuscript:

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As our method of testing the sensitivity of the results has changed from investigating specific scenarios to evaluating the results more generally using a sensitivity analysis, this sentence no longer applies in the updated manuscript.

12. Referee:

Page 6, lines 34-35: Please indicate in the text why Houston sites were selected to obtain NO₂/NO ratios for Detroit. Are NO₂/NO ratios reasonably similar for all urban sites?

Author Response/Changes in Manuscript:

As with the last comment, this comment no longer applies in the updated setup of the study.

13. Referee:

Page 7, line 4: "The Detroit data display...". Please indicate in the text where this data is displayed.

Author Response/Changes in Manuscript:

As with the last comment, this comment no longer applies in the updated setup of the study.

14. Referee:

Page 7, line 12: Please point the reader to Figure S4 at the start of paragraph, rather than midway through. This provides context for the discussion.

Author Response/Changes in Manuscript:

The reference to the Figure S4 has been added to the end of the first sentence in the paragraph.

15. Referee:

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Page 7, lines 14-15: "The model tends to under predict nighttime OH concentrations". Is this after taking into consideration measurement interference?

Author Response/Changes in Manuscript:

The interference involved in the IU-FAGE measurement affected only measured HO₂ concentrations during CABINEX (Griffith et al., 2013). This point is clarified within the section in the updated manuscript.

16. Referee:

Page 8, lines 4-5: It's not apparent how the results support an isoprene-derived measurement interference. The slope is near unity (Figure S5(b)) when the model does not include interfering isoprene RO₂, but less than unity (slope = 0.7) when it does. This would suggest that the interference is negligible.

Author Response/Changes in Manuscript:

In this case, because the isoprene-derived interference has been well-characterized elsewhere (Fuchs et al., 2011; Griffith et al., 2013), we assume that the agreement seen between our model and the measurements in terms of HO₂ concentrations is due to an over-prediction of HO₂ by our model. The fact that the diurnal profiles are so similar (when not including isoprene RO₂) is therefore likely somewhat of a coincidence. We will clarify this fact within the updated manuscript; however, the agreement between our model and measured concentrations of HO_x is still well within the range of previously published models (Lelieveld et al., 2008; Pugh et al., 2010; Stavrou et al., 2010).

17. Referee:

Page 12, lines 29-32: More appropriate to compare your total OA (and not SOA only) with total OA from Delia (2004), as the contribution of SOA to total OA is known (page 12, line 37 and page 13, line 1).

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Author Response/Changes in Manuscript:

We have altered the sentence to compare our SOA+POA with the OA measurements made by Delia (2004).

18. Referee:

Page 13, lines 8-9: Does the difference in photolysis above and below the canopy impact SOA formation? It is not apparent that this has been tested in the sensitivity simulations (Figure S6).

Author Response/Changes in Manuscript:

It is clear that the photolysis of NO₃ impacts SOA above and below the canopy. However, it also is likely that photolysis of oxidation products themselves affects SOA formation. Based on the assumption that the above-canopy radiation is the upper bound, we have included an investigation of how reducing photolysis rates affects SOA in the sensitivity analysis section of the SOA results.

19. Referee:

The authors provide labels for above canopy and below canopy data in panel “(a)” of Figures 2 and S2 that seems to suggest the dark lines are for below canopy data and the lighter lines for above canopy data. If this is the case, the authors should clarify this convention in the figure captions.

Author Response/Changes in Manuscript:

The reviewer’s interpretation of the lines is correct. We have edited the figure captions to clarify the coloring conventions.

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