

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

### **Anonymous Referee #2**

Received and published: 29 July 2016

General Description of the manuscript:

The authors use above- and below-canopy measurements of atmospheric composition and a 0D box model to evaluate differences in the oxidative fate and secondary organic aerosol (SOA) formation of the biogenic volatile organic compounds isoprene and alpha-pinene. The authors find that nitrate (NO<sub>3</sub>) concentrations are higher below the canopy than above, leading to enhancements in first-generation organic nitrate (RONO<sub>2</sub>) concentrations. SOA mass concentrations are also higher below the canopy than above, as the ratio of hydroperoxyl radical (HO<sub>2</sub>) to nitrogen oxide (NO) is higher below the canopy than above.

The article is suitable for publication in ACP, but after major revision.

General Comments:

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→ 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 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 NO<sub>3</sub> and O<sub>3</sub> perturbations change NO<sub>3</sub> is obvious and indicated in Equation (4).

→ 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 RONO<sub>2</sub> and SOA formation above and below a forest canopy.

→ 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?

Specific Comments:

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

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

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- 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.
- Page 3, line 37: Please briefly indicate for the reader what the differences are in BVOC (isoprene and alpha-pinene) reactivity and SOA formation.
- 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.
- 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.
- 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.
- Page 6, line 13: “In the second modeled case...”. What was the first modeled case? This is not systematically presented in the methods section.
- Page 6, lines 34-35: Please indicate in the text why Houston sites were selected to obtain NO<sub>2</sub>/NO ratios for Detroit. Are NO<sub>2</sub>/NO ratios reasonably similar for all urban sites?
- Page 7, line 4: “The Detroit data display...”. Please indicate in the text where this data is displayed.
- 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.
- Page 7, lines 14-15: “The model tends to under predict nighttime OH concentrations”. Is this after taking into consideration measurement interference?
- 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 RO<sub>2</sub>, but less than unity (slope = 0.7) when it

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does. This would suggest that the interference is negligible.

- 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).
- 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).
- 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.

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