Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2020-829-RC2, 2020
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Atmospheric Chemistry and Physics Discussions
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Interactive comment on "Using GECKO-A to derive mechanistic understanding of SOA formation from the ubiquitous but understudied camphene" *by* Isaac Kwadjo Afreh et al.

Anonymous Referee #2

Received and published: 18 November 2020

Afreh et al. present findings from a box modeling study performed on camphene, a monoterpene emitted by vegetation and biomass burning. After validating their model on more well-studied monoterpenes: a-pinene and limonene, they find that camphene has a high potential to form secondary organic aerosol (SOA), which is likely to alter SOA estimates from real-world biomass burning that emits a distribution of monoterpenes.

Although global emissions of monoterpenes are dominated by only a few species (a-pinene, b-pinene, limonene), the remaining monoterpenes that include camphene could play an important role locally and regionally. Yet their oxidation chemistry and

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Discussion paper

ability to contribute to SOA production remains uncertain. Hence this study is well-motivated. In addition, it provides a pathway for a similar analysis to be done on both anthropogenic and biogenic volatile organic compounds (VOCs) for which little experimental data are available to determine their atmospheric impacts. However, for a few key reasons, I found the methods, results, and interpretation to be either incomplete or not accurately described. I believe that while this work has the potential, I cannot recommend publication in Atmospheric Chemistry and Physics at this time. See detailed comments below.

Major comments:

1. Autooxidation and oligomerization: There is strong evidence that many monoterpenes participate in autooxidation reactions to form highly oxygenated organic molecules (HOM) and participate in condensed phase reactions to form high molecular weight oligomers (Bianchi et al., Chemical Reviews, 2019). Although the authors mention that this is not considered in this work, *I believe this is a major shortcoming that has the potential to confound the findings for camphene and its comparison with the findings for a-pinene and limonene*. At the very least, this needs to be dealt with in a simplistic manner. For instance, molar yields leading to HOM could be tied to experimental observations (Ehn et al., Nature, 2014; Jokinen et al., PNAS, 2015) and oligomer formation could be informed by reaction rates in the literature (e.g., Ziemann and Atkinson, Chem. Soc. Review, 2012; Roldin et al., ACP, 2014).

2. Section 2.1: Many of the monoterpene oxidation products are likely to be in the semi-volatile range, which co-exist in the gas and particle phases. Point '(2)' makes it seem like the SOA production was limited to only include low-volatility products that are below a certain vapor pressure (on a related note, it would be nice to specify the vapor pressure in C* units of μg/m3). I don't think that is the case but this needs to be explicitly mentioned. Related to this, how are C* values for all oxidation products calculated? Depending on the method used, how does one think about the uncertainty in the methods used to calculate the C*? The fractional contribution of semi-volatile

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organic compounds to the product distribution is likely to affect the SOA mass yield significantly.

3. Comparison with prior chamber data: While the qualitative comparison offered in Figure 4 with prior chamber data is useful, there are many more reasons than those stated in the first paragraph in Section 3.1.1 (lines 190-209) that could explain the differences between the different studies and those studies and this work. A few of them being: differences in vapor and size-dependent particle wall losses, seeded versus unseeded, differences in total oxidant exposure, NO versus NO2 availability, lights used and photolysis rates, relative humidity and availability of aerosol water, and aerosol acidity. Trying to describe differences in prior data exclusively based on their NOx and OA loading differences as well as commenting that model is able to capture the general behavior, is too simplistic and ignores many of the nuances linked to chamber experiments. This section needs to be significantly expanded if the goal is to demonstrate that the model can capture previous observations of SOA mass yields.

4. Application to wildfire SOA (lines 354-370): I am generally in favor of this analysis but do not agree with the approach used here and the context in which they are presented. How consistent are the VBS parameters between the studies chosen (i.e., Griffin, Pathak, Zhang) and the other studies alluded to earlier in Table S1? *Why were the MCM results from the previous sections not used directly to perform this analysis? My sense is that these could easily be used to develop yield estimates for a-pinene, limonene, and camphene.* Further, the analysis does not seem to accurately represent camphene but only compares estimates using the two different approximations (i.e., camphene = a-pinene or camphene = a-pinene+limonene). The projected enhancements for the different fuels are hence unconstrained. Finally, the work should be presented in the context of other studies that have attempted to model SOA formation from biomass burning emissions and the relative importance of monoterpenes or lack of it to other SOA precursors (e.g., phenols, furans, aromatics). See, for example, the work of Bruns et al. (Sci. Rep., 2016), Ahern et al., (JGR, 2019), and Akherati et

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al., (ES&T, 2020).

5. One key aspect that this study fails to highlight – but one that is quite powerful - is the general approach to thinking about SOA formation from unexplored VOCs. I would recommend that a revision of this manuscript highlight this aspect. Particularly, since camphene, regardless of how it is dealt with, may not be important enough to meaningfully affect the total SOA burden from vegetation or biomass burning.

Minor comments (not exhaustive):

1. Line 53: Reaction rates or reaction rate constants? Having very different reaction rate constants doesn't necessarily mean that the atmospheric lifetimes could vary by the same amount.

2. Introduction: Well-cited section but could perhaps also be motivated by how these monoterpene emissions and their composition could change with future temperatures.

3. Line 86: 'compared'.

4. Section 2.2: How are the generalized reaction schemes for monoterpenes determined?

5. Line 186: Why was 50 degrees selected?

6. For the results discussed in Section 3.1, can time series plots for SOA mass, O:C, and major components be included in the main text or SI for the simulations?

7. Table 3: This only shows modeled O:C values. Can a comparison similar to Figure 4 be also be performed for SOA O:C, in addition to or instead of the comparison to literature values in the second paragraph in Section 3.1.1? On a related note, HOM formation will tend to further increase the modeled O:C and further separate the modeled O:C from the literature data. Thoughts on why this might be? Is this related to not having enough semi-volatile material with low O:C to 'dilute' the bulk O:C?

8. Line 225: It would seem like a lot of H2O would need to be lost (and lot of oligomers

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produced in the process) to explain the differences in the modeled and measured O:C. Can this calculation be done to test plausibility?

9. Line 227: It should have been relatively easy to zero out the OH in the model simulations to appropriately represent the chamber experiments where an OH scavenger was used.

10. Section 3.1.2: The volatility distribution of a-pinene SOA has been well studied (e.g., Saha and Grieshop, ES&T, 2016; Yli-Juuti et al., GRL, 2017) and to some degree its composition too (e.g., Sato et al., ACP, 2018; D'Ambro et al., ES&T, 2018). While a qualitative comparison has been done here, can this be done more quantitatively against literature data? For instance, could the modeled SOA products be lumped by volatility and compared against volatility distributions constructed from analyzing dilution, thermodenuder, and speciation data? Can the modeled composition be compared directly to measured data at the species level? This would help improve confidence in the model predictions.

11. Line 254: Should it be 'macroscopic'?

12. Line 263: Do you see an effect of photolysis on SOA mass yields? This recent study might be of interest to examine for consistency with this work: https://doi.org/10.1021/acs.est.9b07051

13. Line 288: Were these values picked to replicate atmospheric conditions? If yes, this should be stated. Was there a reason the model was not used to explore dependence on T, RH, NOx, etc?

14. Section 3.2: If SOA production was assumed to be instantaneous, would the kinetics under low condensational sink conditions, alter the model predictions significantly under atmospheric conditions?

15. Section 3.2.3: How would HOM production and differences between the three VOCs affect the modeled particle-phase product distribution and its volatility? This

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should have a reasonable impact on the results shown in Figure 11.

16. Line 375: ‘lower than’ what?

17. Line 380: Needs to be made clear that this is only for the SOA contribution from monoterpenes, which could be quite small, depending on the fuel type.

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