

## ***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.***

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2.1: 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:  $\alpha$ -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 ( $\alpha$ -pinene,  $\beta$ -pinene, limonene), the remaining monoterpenes that include camphene could play an important role locally and regionally. Yet their oxida-

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tion chemistry and 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.

No response required.

Major Comments 2.2: 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  $\alpha$ -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).

Response: We agree with the reviewer that HOM formation and subsequent dimerization in the gas-phase is likely to be an important contributor to SOA formation under certain conditions, as has been demonstrated in laboratory, field, and modeling studies. We note HOM formation+dimerization has been particularly studied in the context of new particle formation, and at low SOA mass loadings, both of which are not relevant here. Efforts are underway to develop a SAR to predict HOM formation that is suitable to run in GECKO-A. This is not trivial to achieve, mainly as the H-shift RO<sub>2</sub> reactions would lead to a non-manageable number of species and reactions if treated explicitly.

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Reduction protocols are currently under development to consider these classes of reactions in GECKO-A. A full consideration of HOM formation/dimerization is however not possible at this time. To that end, the following has been added in lines 104-109: Autoxidation, including the formation of highly oxygenated molecules (HOM) in the gas phase (Bianchi et al., 2019; Ehn et al., 2014), is not currently represented in GECKO-A. A SAR to predict the rate coefficients of peroxy radical (RO<sub>2</sub>) H migration reactions (H-shifts) that lead to the formation of HOM, was recently published by Vereecken and Nozière (2020). The straight implementation of this SAR into GECKO-A would lead to a non-manageable number of species and reactions. Reduction protocols are thus currently under development to consider the autoxidation reactions in subsequent model versions. Also, the following revision has been made in lines 125-126: “Condensed-phase reactions are not currently represented in GECKO-A.” Nonetheless, based on the reviewer’s suggestion, we have done some calculations regarding RO<sub>2</sub> lifetimes with respect to different terminal reactions and some estimations of the potential importance of HOM formation + dimerization for SOA formation. Guided by Bianchi et al., 2019 and references therein, RO<sub>2</sub> lifetimes with respect to NO, HO<sub>2</sub>, and RO<sub>2</sub> were calculated for all of the simulation conditions. As has been previously shown and summarized in Bianchi et al. 2019, the lifetime of RO<sub>2</sub> with NO is too short (< 7 s in our simulations) under photooxidation conditions with NO<sub>x</sub> for HOM formation to play a significant role in gas-phase chemistry. Whereas under dark ozonolysis conditions, the lifetime of RO<sub>2</sub> is long enough such that HOM formation may play a role in gas-phase chemistry and SOA formation. Calculations of gas-phase HOM and HOM-dimer yields as a function of time are qualitatively consistent with Ehn et al., that at the beginning of the simulations (for the fastest assumed rate constant), where RO<sub>2</sub> concentrations are highest and SOA mass concentrations are lowest, HOM dimers likely contribute to SOA mass and may result in an increase in the predicted SOA yield. However as the SOA mass increases in time, the contribution of such dimers is outweighed by the contribution of more abundant SVOCs. That RO<sub>2</sub> dimerization may contribute to SOA formation at the beginning of the dark ozonolysis (DO) chamber condition simulations

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does not change the key discussion points or conclusion of the manuscript. Of more relevance are the controlled reactivity simulations, which were designed such that RO2 reacts  $\sim$ equally with HO2 and NO. The lifetime of RO2 is  $< 60$  s in such simulations, and thus, we do not expect RO2 HOM formation and dimerization to significantly affect the gas-phase chemistry or SOA formation. Further, given the range of HOM yields as a function of reaction conditions and parent compound structure, and the lack of available information for camphene, efforts to calculate HOM formation, dimerization, and SOA formation in these simulations would be overly speculative and would not likely contribute any concrete findings on the importance of such chemistry, particularly for camphene. Regarding heterogeneous/particle-phase accretion reactions, in McVay et al. 2016 particle-phase dimerization was considered for three reactions using two different rate constants, and the results were compared with chamber studies. For both high and low UV conditions the predicted SOA yield increased; while this improved measurement-model agreement for the low UV experiments, it resulted in a significant over prediction in the high UV experiments. For the chamber simulation conditions in this work, the time-dependent product distributions (by functional group) were similar for alpha-pinene and limonene, suggesting that the inclusion of accretion reactions may also increase the simulated alpha-pinene and limonene SOA yields in this work. Similarly to McVay et al., this would likely improve measurement-model agreement in some cases (e.g., alpha-pinene ozonolysis) but not others. Though as noted here and in the manuscript, the goal was not to reproduce any one chamber experiment and a comprehensive suite of sensitivity studies for potentially relevant processes is out of the scope of this work. For the controlled reactivity conditions, no published study exists from which we may draw insight. As with the chamber simulations, the monomer building blocks are present in the particle phase, but simply calculating an accretion yield for these monomers based on published accretion reaction rates is not reasonable because the subsequent gas-particle partitioning can't be considered as it was in McVay et al. 2016. The large number of gas- and particle-phase species ( $9.3 \times 10^4 - 2 \times 10^5$ ) precludes running simple "offline" or out of GECKO-A box models. Modify-

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ing the GECKO-A source code to treat accretion reactions is beyond the scope of this work. We acknowledge that it may be important, and will continue to work on a feasible way to consider such reactions in GECKO-A. In acknowledgement of these important comments, the following sentence has been added to the conclusions (lines 407-408): “The SOA mass, yields and product volatility distributions can also be influenced by gas-phase HOM formation and dimerization, and accretion reactions, which were not considered here.”

2.3: 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  $\mu\text{g}/\text{m}^3$ ). 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 organic compounds to the product distribution is likely to affect the SOA mass yield significantly.

Response: Because we have specific product structures available, vapor pressures are calculated for each compound using the vapor pressure estimation method of Nannoolal, and it is the saturation vapor pressures (and not saturation vapor concentrations,  $C^*$ ) that are used to calculate the partitioning between the gas and condensed phase. A number of studies have been published comparing vapor pressure estimation methods, and the effects of uncertainties on partitioning predictions. For example, Valorso et al. (2011) compared several estimation methods of saturation vapor pressures for secondary organic compounds formed during a-pinene oxidation. As is noted by the reviewer, partitioning of the semi-volatile compounds may be particularly affected by such uncertainties. For a-pinene oxidation, it has been shown that a better measurement-model agreement is obtained when the Nannoolal method is used, es-

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pecially under high NO<sub>x</sub> conditions (e.g. Valorso et al. (2011)). This method is thus recommended for saturation vapor pressure estimation in GECKO-A. Based on the reviewer comments, the following additions or revisions have been made. Lines 124-125 "... which performs relatively well compared to other estimation methods when used to simulate SOA formation during  $\alpha$ -pinene oxidation experiments (Valorso et al., 2011)." Lines 114-116 have been revised as follows: "... species with saturated vapor pressure below 10-13 atm (equivalent to C\* of  $1.02 \times 10^{-3} \mu\text{g m}^{-3}$  for species with a mean molecular weight of 250 g mol<sup>-1</sup>) were considered non-volatile and therefore treated as end products during gas-phase mechanism generation;" Also, a sentence describing the C\* calculation has been added in lines 344-345: "C\* was calculated based on the equilibrium absorption coefficient equation, as defined by Odum et al. (1996) and Pankow (1994)."

2.4: 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 NO<sub>2</sub> 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 NO<sub>x</sub> 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.

Response: We agree with the reviewer and recognize that a large number of factors influence SOA mass concentrations and yields observed in chamber studies. One of the reasons we compiled data from 12 different studies was to account for a range of wall loss effects (as influenced by initial conditions, including seed concentrations, and

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chamber size), temperature and relative humidity (though the vast majority of studies are conducted under dry (< 10% RH) conditions), light intensity, etc. We note in the manuscript that the scatter in the experimental yield data shown in Fig. 4a is due to differences in experimental conditions. We do not attempt to reproduce any individual experiment (and note this in line 183: Here, no attempt is made to strictly reproduce the conditions of a given chamber experiment.). Rather we are evaluating whether the model captures general trends in SOA yields and products, to the extent the latter can be evaluated. We believe that the analysis presented supports the conclusion that the model represents the chamber data (at macroscopic and molecular levels) sufficiently well that it is reasonable to use GECKO-A to probe the potential for camphene to form SOA, relative to alpha-pinene and limonene.

2.5: 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 al., (ES&T, 2020).

Response: The results of the GECKO-A modeling simulations are used to guide this analysis, from the perspective that they indicated that camphene may be represented

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by a mix of alpha-pinene and limonene. The benefit of using these compounds to represent camphene, is that experimentally-based SOA parameterizations are available for such compounds, and are not available for camphene. (In line 358-359, the following has been added: for which SOA parameterizations currently are available.) The GECKO-A modeling simulations do not cover sufficient parameter space to develop a robust SOA parameterization. There are certainly differences in SOA modeling parameters due to differences in experimental conditions (see for example Barsanti et al., ACP 2013). The Griffin et al. parameters were chosen because of their use in the EPA chemical-transport model CMAQ. The Griffin et al. parameters represent a two-product model approach; to illustrate that different parameterizations will give different approximations, a set of VBS parameters was also used. We are not making any claims about the contribution of monoterpenes to BB-derived SOA relative to other BB-derived compounds. We are only demonstrating that for this given emissions source, and this given class of compounds, predictions of SOA may be significantly underestimated using alpha-pinene or “average” terpene SOA yields when camphene represents a significant fraction of the emissions (e.g., black spruce and Douglas fir).

2.6: 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

Response: We agree! This is beyond the scope of this manuscript, but it is the focus of a subsequent manuscript that is in preparation.

Minor Comments 2.7: 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.

Response: We agree. “Reaction rates” was changed to “reaction rate constants” and

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the text revised in lines 53-55: “The reaction rate constants of monoterpenes with atmospheric oxidants vary by orders of magnitude (Atkinson and Arey, 2003a; Geron et al., 2000), and their atmospheric lifetimes vary from minutes to days (Atkinson and Arey, 2003b).”

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

Response: This is a very good point, though currently, we don't think that there is enough known about how such emissions will change in the future. While there have been many efforts to quantify this change, it has often been in the absence of other expected changes (e.g., levels of CO<sub>2</sub>, ozone, etc.), which also can affect emission rates.

2.9: Line 86: ‘compared’.

Response: This has been corrected.

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

Response: A brief description of the generation of reaction schemes using GECKO-A has been in lines 128-134.

2.11: Line 186: Why was 50 degrees selected?

The simulation conditions were selected to represent mean typical chamber. Mean photolysis conditions were thus calculated using a zenith angle of 50°. The details have been added to the sentence line 202-203: “the solar zenith angle, required to calculate photolysis frequencies, was set at 50° to represent mean daytime solar spectra.”

2.12: 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?

Response: Time series plots for SOA mass, O:C, and top 10 products now have been

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included in the SI.

2.13: 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?

Response: As noted above, we do not expect HOM formation/dimerization to contribute significantly to the final SOA mass/yield observed in these studies. Though we do agree that if such compounds were important in the dark ozonolysis studies, this would further separate the measured and modeled O:C ratios. The literature-based observed O:C ratios, where available, have now been included in Table 3.

2.14: Line 225: It would seem like a lot of H<sub>2</sub>O would need to be lost (and lot of oligomers produced in the process) to explain the differences in the modeled and measured O:C. Can this calculation be done to test plausibility?

Response: This is a good point. The recommended calculation indicates that ~50% of mass would need to be oligomers to explain the difference in O:C. Prior GECKO-A modeling-chamber comparisons (McVay et al., 2016) indicated that SOA yields increased significantly when accretion reactions were included, particularly when the faster rate constant was used. It is likely that the addition of accretion reactions would improve O:C agreements, but then may also result in overprediction of SOA mass relative to the chamber experiments (particularly for limonene, and without considering some loss processes). We have modified the sentence slightly to reflect the possibility but also uncertainty (lines 243-244): "Therefore, the lower observed O/C values may be partially explained by the loss of H<sub>2</sub>O during oligomerization, ...".

2.15: 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

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was used.

Response: As suggested by the reviewer, sensitivity studies were run in which CO was used as an OH scrubber. The predicted O:C ratios were not significantly different between the sets of simulations, and thus this sentence has been removed.

2.16: 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.

Response: Quantitative comparisons of GECKO-A simulations with a-pinene chamber experiments for the purpose of SOA formation has been performed by Valorso et al., 2011; Denjean et al., 2015; McVay et al., 2016. These studies mainly focus on model/measurement comparisons of SOA mass and/or O:C ratio. A quantitative model/measure comparison on volatility distributions and/or gaseous and particulate individual species would indeed provide additional confidence in the model simulation, and allow to improve our knowledge of processes in particular those leading to HOM formation. Such a quantitative comparison can for sure be the objective of a paper but is out of the scope of the study presented here.

2.17: Line 254: Should it be 'macroscopic'?

Response: This has been corrected.

2.18: 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:

Response: We agree with the reviewer that representing loss processes are important, particularly when trying to match ambient observations or make atmospheric predictions. Gas-phase photolysis is represented in GECKO-A (including the current work), and particle-phase photolysis in GECKO-A has been explored by Hodzic et al. 2015. That said, the consideration of loss processes, including particle-phase photolysis, is beyond the scope of this work.

2.19: 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, NO<sub>x</sub>, etc?

Response: As noted in the manuscript, the controlled reactivity conditions represent conditions in which the gas-phase chemistry is not controlled by the individual hydrocarbons, as is true in the atmosphere. However, this is not the same as being relevant for atmospheric conditions, which cover large ranges in terms of the controlling variables. An exhaustive sensitivity study of the formation of camphene SOA as a function of all of the controlling variables is beyond the scope of this work.

2.20: 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?

Response: The assumption of instantaneous equilibrium would not likely affect SOA predictions under atmospheric conditions unless the temperature/relative humidity/OA composition were such that the particles were viscous. It is under such conditions, or for consideration of new particle formation, that SOA formation needs to be treated kinetically.

2.21: 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.

Response: While the overall mass loadings are low enough in the controlled-reactivity simulations that HOM formation/dimerization could have a non-negligible contribution to the particle phase composition, the relatively short lifetimes of RO<sub>2</sub> (< 60 s) in these simulations suggest that HOM formation is relatively unimportant. In the event that HOM formation did occur, since HOM yields for limonene are typically higher than alpha-pinene, the difference in the % of E/LVOCs contributing to the particle-phase would be further magnified. No HOM yields have been published for camphene so it is unclear how the particle-phase volatility distribution would change, should HOM formation occur.

2.22: Line 375: 'lower than' what?

Response: This has been corrected and now reads (line 399): "...lower than oxidation products predicted for  $\alpha$ -pinene and limonene."

2.23: 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.

Response: Agreed. The clause "from monoterpenes" has been added to line 404.

Please also note the supplement to this comment:

<https://acp.copernicus.org/preprints/acp-2020-829/acp-2020-829-AC2-supplement.pdf>

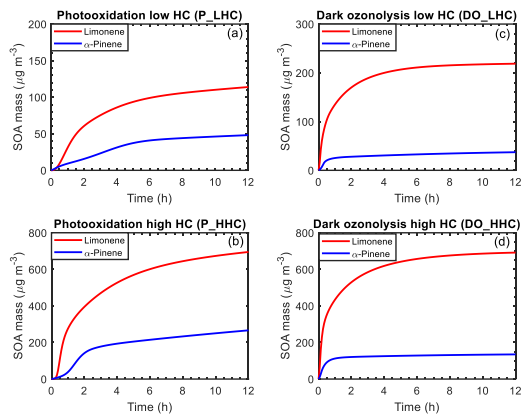
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Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2020-829, 2020>.

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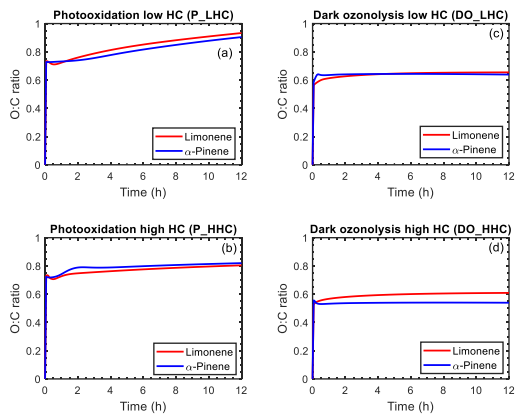
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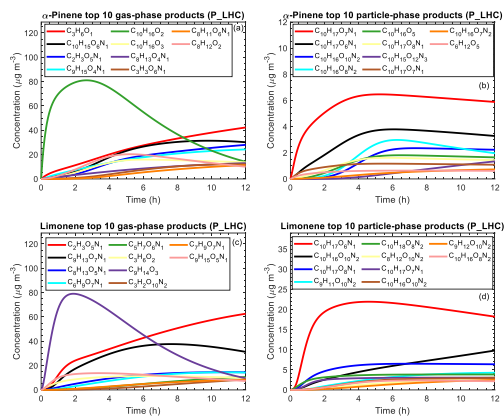
**Fig. 1.** Figure S14: Simulated SOA mass as a function of time for  $\alpha$ -pinene and limonene during photooxidation and dark ozonolysis with low hydrocarbon mixing ratio (50 ppb).

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**Fig. 2.** Figure S15: Simulated average O/C as a function of time for  $\alpha$ -pinene and limonene during photooxidation and dark ozonolysis with low hydrocarbon mixing ratio (50 ppb).

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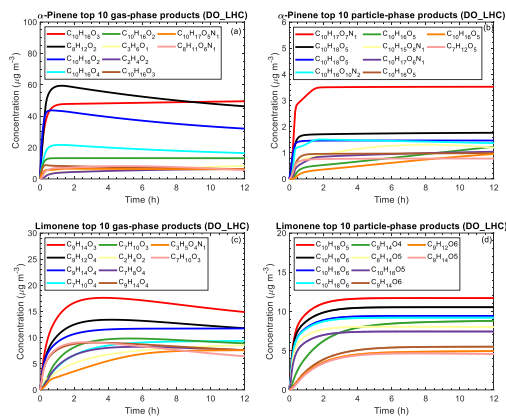
**Fig. 3.** Figure S 16: Concentration of top 10 gas- and particle-phase products as a function of time for  $\alpha$ -pinene and limonene during photooxidation with low hydrocarbon mixing ratio (50 ppb).

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**Fig. 4.** Figure S 17: Concentration of top 10 gas- and particle-phase products as a function of time for  $\alpha$ -pinene and limonene during dark ozonolysis with low hydrocarbon mixing ratio (50 ppb).

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