Comment on "Modeling Diurnal Variation of SOA Formation via Multiphase Reactions of Biogenic Hydrocarbons"
Anonymous Referee #1

Referee comment on "Modeling Day and Nighttime SOA Formation via Multiphase Reactions of Biogenic Hydrocarbons" by Sanghee Han and Myoseon Jang, Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2022-327-RC1, 2022

The manuscript “Modeling Diurnal Variation of SOA Formation via Multiphase Reactions of Biogenic Hydrocarbons” presents an attempt to model SOA formation from three different VOC precursors under various conditions and to validate those results with chamber experiments. To do so, the authors have extended their own UNIPAR model with additional oxidation pathways and reactions including product lumping based on volatility. In addition, physical parameters like relative humidity, temperature, etc. from the chamber experiments have been used as conditions for the model simulations.

The paper presents some interesting science and an approach that is well worth publication in ACP after major revisions and corrections.

General remarks:

- The authors should try to improve the language of the manuscript to increase its readability and help the reader to understand it more clearly. One common mistake to be found throughout the manuscript is the use of the direct article or its omission in the wrong places. I recommend careful proofreading by a native speaker (of the revised manuscript!).
- The title suggests investigation of the complete diurnal cycle. The experiments for individual compounds however do not cover whole day cycles but limited periods (3-12 h total, 2-10 h for VOC oxidation/chemistry). In most cases, these periods even differ for different compounds/experiments. Therefore, I recommend changing the title to “… under day- and nighttime conditions …” or similar.
- The abstract is quite long and detailed and partially feels like a conclusion. It might be good to shorten it slightly to give the audience the motivation to read the paper!
- In several places, the authors mention that modeling the gas phase chemistry was done using explicit mechanisms, at other places, the talk about “near explicit mechanisms”.
These expressions are quite ambiguous without clear statements what the authors mean by explicit at the time of use (kinetics, mechanism, et cetera). This is especially true since it is mentioned (in some parts) that the resulting products were lumped based on their volatility, preventing for example explicit modeling of 2\textsuperscript{nd} and higher generation products. I recommend to either rephrase or clarify the extent of this “explicit modelling”.

- Often the authors tend to mix introduction, background, results, and discussion throughout the whole manuscript leading to repetitive statements and elongating it unnecessarily. The manuscript would gain a lot quality wise by clearly separating these different parts (both in term of length and readability).
- Some parts of the manuscript seem to be more a review paper than an original work. Again, a more in-depths presentation and discussion of the results of this work would be very beneficial for the manuscript.
- Many of the plots and diagrams are very small, and the axes are unfortunately scaled. This makes it really difficult to follow the authors discussion of their results! The graphical presentation of the results should also be improved!

Individual comments:

P1 L9: “... intensively evaluated ...”: I suggest removing “intensively”. It is an unnecessary exaggeration.

P1 L13: How can the gas mechanism implement the MCM? Please rephrase!

P1 L15: How did integration with the SAPRC gas mechanism “increase feasibility”? Please clarify or rephrase.

P1 L21: What are background NO\textsubscript{x} levels in the simulation (and the chamber experiments)?

P1 L30: What is the meaning of “…more sensitive to the aqueous reactions...” Please clarify.

P1 L32: “Diurnal patterns” cover the whole daily cycle! Your experiments do not comply with this definition.

P2 L40: Organic aerosol is not a “well-known” factor – that is why research on this topic is so important. Please rephrase!
P2 L42: SOA is in general important number wise, but for mass mostly in the PM1 range!

P2 L47: “The SOA from ... is considerable in a global budget of SOA.” Please rephrase, there is only one global SOA budget!

P2 L50: “… HC is oxidized mainly with OH radicals …” Is this still true in the presence of high concentrations of NOₓ?

P2 L54: Ozone is normally not persistent during night times but destroyed by chemical reactions. Only when it is lifted above the boundary layer (e.g., by an inversion layer) can it survive until the next morning. Otherwise, tropospheric ozone concentration would continue to rise. Please rephrase!

P2 L64: What is “absorbing organic matter concentration”? Please clarify.

P2 L65: “The oxidation ... was approached by ...”: Please rephrase.

P2 L67: What do you mean by “were not additive”?

P2 L74: “inorganic salted aqueous phase”: An aqueous solution is by definition a solution of a chemical in water, often of an inorganic salt. I guess what you want to say is “aqueous phase of inorganic salts”. This expression “salted aqueous phase or solution” is several times used throughout the manuscript. I recommend changing it.

P2 L78: “This model has been demonstrated by ...” I believe this sentence is incomplete.

P3 L 82: “…were generated from the four different ... pathways” How were they generated from the pathways? Rephrase!

P3 L 83: “To improve the feasibility ..., providing the HC consumption by each oxidant” This sentence is in parts an exact replication of the sentence in the introduction, and again it does not make too much sense. Please clarify. Also, a citation for the SAPRC-07TC mechanism would appropriate.
P3 L86: “The potential SOA yield(s) ... were applied” Applied to what? Please rephrase!

P3 L97: “... injected from a 2% NO cylinder under the air flow ...” What do you mean by under the airflow? Please clarify!

P3 L99: How did you ascertain that the sulfuric acid seeds were not neutralized during injection? It is quite a task to prevent its neutralization by ammonia which is very abundant.

P3 L102: What do you mean with “NOx condition was controlled by NO2“?

P3 L113: “The inorganic ion ... concentrations were in situ monitoring by ...” should be “... in situ monitored by a Particle-Into-Liquid-Sampler ...”

P3 L115: The use of butanol-based CPCs in chamber studies is quite controversial because of potential contamination. Did you check for this?

P3 L119: “An Aerosol Chemical Speciation Monitor ... to compare with data obtained from OC/EC and PILS-IC for accurate measurements.” Each of these methods have their own uncertainties; therefore, I would avoid the term “accurate measurements”.

P3 L119: “The relative humidity and temperature were monitored ...” How was this done (at how many different locations)? Since your chambers are quite large there could be a temperature (and humidity) gradient inside of it.

P3 L120 (also P1 L9): “... sunlight intensity was measured by Total Ultraviolet Radiometer.”? The results of these measurements are not presented in Table1 but could be important for the chemistry and the SOA mass yield!

P3 L120: Why are the results of the aerosol acidity measurements not presented in Table 1? This could also help to answer the question regarding sulfuric acid neutralization.

Follow up: In the beginning the authors speak of sulfuric acid seed particles, in the later parts they only mention ammonium bisulfate (which is to be expected). This should be clarified and correctly be mentioned right from the beginning.
P4 L124: Again, explicit to which degree? Which mechanisms were used (reference)?

P4 L127: “… were determined by the near-explicit gas mechanism.” Which mechanism?

P4 L134: “… salted aqueous solutions …” How were they salted? Sodium chloride, ammonium sulfate, or something different?

P4 L135: What is the relation between liquid-liquid-phase-separation and isoprene SOA formation and condensation on inorganic seed particles, and why did you exclude it? An explanation (and maybe a citation?) for the general reader would be nice.

P4 L117: What do you mean by “was included to fulfill the oxidation mechanism in the current regional model”?

P4 L157: “$a_i$ ... was estimated by the predetermined mathematical equation originated from the explicit mechanism as a function of ...” This sentence is difficult to understand. What is “$a_i$”? Are these the elements of the unified array calculated for each hydrocarbon oxidation pathway? Please elaborate!

P5 L169: $OM_T$ is only introduced on P6 L222.

P5 L171: “... is also calculated as the traditional ...” should be “... according to the ...” or similar.

P5 L209: Many phrases and statements are repeated again and again throughout the manuscript with nearly the exact wording, for instance here the “predetermined mathematical equations”, and “lumping species generated from the explicit mechanism”. The manuscript would gain a lot if those repetitions would be minimized, and the description of the mechanism development would be much more comprehensible for the reader.

P6 L230: “Thus, the seed effects observed in the presence of NO$_x$ ...” This sentence is really difficult to understand. Do you want to say that the presence of NO$_x$ had no influence on the SOA formation in the presence of seeds? What are those “seed effects”?

P7 L243: Which large molecules and how did you measure them? And even if they have a
poor solubility, couldn’t the aerosol acidity still be important in a liquid organic phase?

P7 L245: Why do you mention that isoprene products can be “mixed” with aqueous solutions of inorganic salts, when you did exclude this, as mentioned in the previous sentence?

P7 L270: First you mention that your results show that for isoprene OH is the most important oxidant and that this agrees with previous studies, then you write that reaction with ozone is only minor, only to conclude (again) that your results suggest that a sizable fraction (whatever that is) of isoprene SOM is formed via the OH pathway.

P7 L263: The whole paragraph about the α-pinene simulations has only one sentence that discusses your results. All remaining parts are statements and knowledge from references, which belong rather into the introduction and not in a result/evaluation section if not put into a direct context with your simulations. What is missing here would be for example a discussion why for most cases there is no significant difference between low and high humidity (besides the ammonium bisulfate/acidic seed cases).

P8 L272: Have you investigated the amount of photo degradation of β-caryophyllene and the resulting products in your simulation to be able to calculate their volatility or is this a speculation or scientific knowledge (citation!)?

P8 L279: Throughout the document you often equate NOx with the NO3 radical, which can be done in parts at nighttime in the presence of ozone. However, during daytime jNO2 might play an important role which could even terminate certain oxidation pathways (of VOCs) resulting in higher volatility organic nitrates in the gas phase and thus less SOA. Again, this paragraph consists in large parts of repetition and citation of literature without direct context to your results and does not really discuss the results of the simulation.

P8 L303: “The simulation of ... is performed with ... In the presence of the chamber wall” – Do you mean to say that wall effects were included in the model? Please rephrase!

P8 L306: “Overall, the effect ...” Any suggestions why that could be the case?

P9 L317: Why did you choose those VOC concentrations? They seem quite high compared to typical values, especially in the urban atmosphere.

P9 L318: “The sensitivity of SOA mass ... is simulated ...” should be “... is/was
investigated by simulating ...”. Why are the results of this simulation only shown in the supplementing material and not discussed here?

P9 L321: This paragraph repeats just the results presented in 4.2.

P9 L324: “In addition, OH radical’s contribution ... is positively correlated to ozonolysis, which produces OH radicals as a byproduct.” This is a recursive statement and should be removed or rewritten.

P9 L 342-345: This is nearly a 1:1 repetition of L316-319 ...

P9 L347: “In nighttime, the simulation suggests ... at the high NOx zone due to the high SOA potential ...” What is a NOx zone? Please rephrase sentence!

P10 L360: What kind of gasoline fuel was used? And why this concentration? Is this relevant for the real atmosphere or is it just a simulation experiment. If it is relevant, what are common concentrations of gasoline fuel in the (urban?) atmosphere?

P10 L365: How was the oxidation of the gasoline fuel implemented? If it was not implemented comparable to for example the α-pinene (tegarding mechanisms and chemistry) it could also explain why it did not contribute to the SOA formation in the simulation.

P10 L370: It has long been known that aromatic compounds can be efficient OH scavengers

P10 L381ff: The discussion of results from section 4.5 is effectively missing. It is hinted, that α-pinene SOA formation showed the strongest reaction to the changes of the model parameters, and that the change of the partitioning coefficient had the largest impact on the three biogenic SOA formation systems, but nothing more. Therefore, this section should be either extended or removed.

P10 L386: Why was a different relative humidity used in these simulations?

P11 L394ff: Maybe “Conclusions” would be more fitting to this section!
P11 L411: "... under high NOx zones ..." should be "concentrations" or "levels".

P11 L412: "Under the rural environment" should be "In rural environments" or "In a rural environment".

P11 L415: Nearly all soluble inorganic and organic salts are electrolytes.

P11 L419ff: "In this study ... showed a weak seed impact ..." How is this related to the previous statement about acidic seeds in other studies? Rephrase!

P11 L428: "... showing the higher biogenic HC emission" should be "showing higher biogenic HC emission(s)".

P11 L429: Why is the "concentration of NO2 generally high" during daytime? If there is no source of NO and no ozone, where is it supposed to come from? Rephrase the sentence!

P12 L435: "The model uncertainties ... mainly originate from gas mechanisms and aerosol phase reactions." What other factors are important for SOA formation besides gas and aerosol phase? Please rephrase.

P12 L440ff: "Neither ... nor ... were not fully considered" In this context a double negation does not affirm but resolves to a positive. Rephrase!

P12 L447: The manuscript ends abruptly. There should be some final remarks or conclusions.

P17 Table 1: Why were such huge isoprene concentrations used for the experiments? I do not believe isoprene concentrations of 700 ppbC (140 ppbV) and above are of any atmospheric relevance. And even under such high hydrocarbon concentrations I would not consider 50 ppbV NOx to be a low NOx case!

P17 Table 1: I am quite surprised by mass yields as high as 157 µg per cubic meter from 84 ppbC (8.4 ppbV) a-pinene, especially without any seed (AP01).
P20 Figure 2: The caption claims to present OM\_T and OM\_AR (dotted line), while the
legend annotates the dotted line as OM\_p

P22 Figure 4: It is difficult to distinguish between O(3P) and OH

P23 Figure 5: All plots are too small. In addition, the axis of (a) suppresses the view of the
dynamics in the plot. While it is in general a good idea to scale plots similar this should
not hinder the interpretation of the diagrams.

P23 Caption: What does “the reference sunlight intensity” mean? Is this the total intensity
of the sunlight at that specific day, or is it a wavelength dependent intensity (plot), and
why did you choose this specific date? How does it compare to the average sunlight
intensity at this place, and at other places? This is a very arbitrary measure which modern
science tries to and should avoid. Please reason why you chose this day and intensity
spectrum.

P24 Figure 6: Like Figure 5 all diagrams are way too small. Again, the scaling of the y-axis
of the isoprene plot makes it impossible to clearly see any dynamic factors.