

Modeling Diurnal Variation of SOA Formation via Multiphase Reactions of Biogenic Hydrocarbons (Manuscript Ref#: acp-2022-327)

Response to the Referee1

We would like to thank the reviewer for their time and thoughtful comments on this manuscript. Their comments are repeated below followed by our response to each comment.

Overall Comment on the manuscript

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:

- a. 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 proof reading by a native speaker (of the revised manuscript!).
- b. 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, 2-10h 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.
- c. 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!
- d. In several places the authors mention that modeling the gas phase chemistry was done using explicit mechanisms, at other places they 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 2nd and higher generation products. I recommend to either rephrase or clarify the extent of this “explicit modelling”.
- e. 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 of quality by clearly separating these different parts (both in terms of length and readability). Some parts of the manuscript seem to be more a review paper than an original work. Again, a more in-depth presentation and discussion of the results of this work would be very beneficial for the manuscript.
- f. 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!

Response

- a. Both the language of the manuscript and the flow have been improved to help the reader to provide clear description.
- b. In order to response to the reviewer, the title of the manuscript has been changed from “Modeling Diurnal Variation of SOA Formation via Multiphase Reactions of Biogenic Hydrocarbons” to “Modeling day and nighttime SOA formation via Multiphase Reactions of Biogenic Hydrocarbons” in the revised manuscript
- c. Abstract has been modified to provide better flow in the context and concise.
- d. Words “near explicit mechanisms” were replaced with “explicit mechanisms” in the revised manuscript.
- e. Both the language of the manuscript and the flow have been improved to help the reader to provide clear description.
- f. Figures have been revised with a larger frames and characters.

Individual comments:

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

Response: The manuscript has been revised based on this comment. “intensively” is removed from the manuscript.

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

Response: The manuscript has been revised based on this comment. The gas oxidation process has been simulated by including MCM, PRAM, and formation of low volatile compounds.

L13: “The gas mechanisms include the Master Chemical Mechanism (MCM v3.3.1), the reactions that formed low volatility products via peroxy radical (RO₂) autoxidation, and self- and cross-reactions of nitrate-origin RO₂.”

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

Response: This sentence has been removed from the abstract in the revised manuscript.

4. P1 L21: What are background NO_x levels in the simulation (and the chamber experiments)?

Response: The background NO_x level was low as ~3 ppb before experiment. For the experiment, the NO_x levels varied based on the chamber conditions. HC/NO_x levels were classified into two groups, low NO_x (HC/NO_x < 5 ppbC/ppb) and high NO_x (HC/NO_x > 5 ppbC/ppb) as seen in Table 1. The simulation was performed under the same conditions with experiment to predict chamber-generated SOA data. The HC/NO_x ratio was set as 3 ppbC/ppb for high NO_x conditions and 10 ppbC/ppb for low NO_x conditions for the sensitivity or uncertainty tests.

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

Response: The daytime SOA mass was more influenced by aqueous phase reaction, compared to that in nighttime. To make it clear, the manuscript has been revised based on this comment.

L28: “The daytime SOA formation was generally more sensitive to the aqueous reactions than the nighttime SOA because the daytime chemistry produced more highly oxidized multifunctional products.”

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

Response: The “Diurnal patterns” is replaced with the “sunlight intensity” in the revised manuscript according to this comment.

7. P2 L40: Organic aerosol is not a “well-known” factor – that is why research on this topic is so important. Please rephrase!

Response: “well-known” has been removed in the manuscript based on this comment.

8. P2 L42: SOA is in general important number wise, but for mass mostly in the PM1 range!

Response: To make it clear, the manuscript has been revised based on this comment.

L36: “A large portion of organic aerosol, especially of the fine particulate matter, is secondary organic aerosol (SOA) produced from the oxidation process of hydrocarbons (HCs), emitted from both biogenic and anthropogenic sources”

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

Response: The manuscript has been revised based on this comment.

L43: “Furthermore, the SOA from the oxidation of biogenic HCs is a considerable source of the global SOA budget (Kelly et al., 2018;Hodzic et al., 2016;Khan et al., 2017).”

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

Response: Yes. In daytime, the photolysis of NO₃ radical in the ambient air will be fast enough to consume the NO₃ radical with little reaction with hydrocarbons.

11. 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!

Response: After sundown, O₃ is not rapidly and completely consumed as is the OH radicals. To make it clear, the manuscript has been revised based on the comment.

L51: “The O₃ generated in daytime is not rapidly consumed at nighttime and can react with NO₂ to form a NO₃ radical that can also be sustainable in nighttime.”

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

Response: This sentence has been moved to P2 L70 and relocated in the revised manuscript. Now reads,

L70: “The typical SOA models that are semi-empirically established a relationship between the organic matter (OM) concentration and the SOA yields by using simple partitioning parameters for two (Odum et al., 1996) or more surrogate products (Donahue et al., 2006) include organic-phase oligomerization, but they do not fully treat the SOA formation via the aqueous reactions in the presence of inorganic salts.”

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

Response: The manuscript has been revised based on this comment.

L59: “The biogenic SOA formation in current air quality models is predicted with the surrogate products originating from four major oxidants: OH radicals, NO₃ radicals, O₃, and O(³P).”

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

Response: Due to the cross reactions, the gas phase reaction could be dynamic and hard to constrained by specific oxidation path. To make it clear, the manuscript has been revised based on this comment.

L60: “However, the gas phase reactions cannot be constrained by a specific oxidation path due to the various cross reactions with major oxidants.”

15. 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.

Response: “inorganic salted aqueous phase” is replaced by “inorganic salt” or “aqueous phase of inorganic salts” in the revised manuscript.

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

Response: This sentence was moved to P2 L75 and revised based on this comment as below:

“This model was demonstrated by simulating the SOA formation from various aromatic HCs (Im et al., 2014;Zhou et al., 2019;Han and Jang, 2022), monoterpenes (Yu et al., 2021), and isoprene (Beardsley and Jang, 2016).”

17. P3 L 82: "...were generated from the four different ... pathways" How were they generated from the pathways? Rephrase!

Response: The model parameters were produced for the oxygenated products estimated by simulating the gas mechanisms under the various NO_x levels (1~50 ppbC/ppb). To make it clear, the manuscript has been revised based on this comment as below:

"Lumping species and their stoichiometric coefficient and physicochemical parameters from the explicit gas mechanisms were individually obtained from the four different oxidation pathways with OH radicals, O₃, NO₃ radicals, and O(³P)."

18. P3 L83: "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 SAPRC07TC mechanism would appropriate.

Response: This sentence has been removed from the revised manuscript.

19. P3 L86: "The potential SOA yield(s) ... were applied" Applied to what? Please rephrase!

Response: The manuscript has been revised based on this comment.

L80: "The potential SOA yields of biogenic HCs via four different oxidation paths were simulated by using the UNIPAR model and utilized to study day and nighttime patterns in biogenic SOA formation under varying NO_x levels, temperature, and seed conditions."

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

Response: The NO and NO₂ were injected from the cylinder through the clean air stream. To make it clear, the manuscript has been revised based on the comment.

L91: "NO was introduced into the chamber from the NO cylinder (2%, Air gas) prior to sunrise for daytime experiments. The NO_x level is classified into the high NO_x level (HC/NO_x < 5.5 ppbC/ppb) and the low NO_x level (HC/NO_x > 5.5 ppbC/ppb) based on the initial concentrations of HC and NO."

21. 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.

Response: Sulfuric acid could be neutralized during both injection and experiment. Thus, the inorganic concentrations (SO₄²⁻, NH₄⁺, and NO₃⁻) of aerosol were monitored by using PILS-IC from the beginning of the experiment. The FS values, which is the SO₄²⁻ to NH₄⁺ ratio, were presented in the figures and Table 1, suggesting the aerosol acidity.

22. P3 L102: What do you mean with "NO_x condition was controlled by NO₂"?

Response: To have the targeted NO_x condition for the nighttime experiment, NO₂ was injected instead of the NO to produce NO₃ radical from the reaction between NO₂ and O₃. The sentence was rewritten to better understand for the reader.

L96: “O₃ was injected first into the chamber by using the O₃ generator (Jenesco Inc) followed by the NO₂ injection by using the NO₂ cylinder (2%, Air gas). Nighttime biogenic SOA formation was observed under the three different NO_x levels (i.e., O₃ only, low NO_x (HC/NO_x > 5.5 ppbC/ppb) and high NO_x level (HC/NO_x < 5.5 ppbC/ppb)).”

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

Response: “monitoring “ has been replaced with “monitored” in L107.

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

Response: We aware this problem. After each chamber experiment, we disconnect SMPS from chamber. In addition, the UF-APHOR chamber is located on the roof of the Black Hall and thus, separated from the laboratory air. Prior to the chamber experiment, the chamber background air is monitored to ensure negligible contamination by other trace gases.

25. 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”.

Response: “for accurate measurements” has been removed in this sentence.

26. 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.

Response: The relative humidity and temperature were monitored by the sensor inside each chamber. However, the gradient of temperature or humidity inside of the chamber was not considered in this study.

27. 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!

Response: The sunlight intensity can influence on the SOA mass yield as referee mentioned above. To indicate the sunlight intensity for each experiment, Table 1 has been updated in the revised manuscript as below:

Exp. ID	Date	Initial condition				FS	Temp (K)	%RH	max OM (μg m ⁻³)	Max TUV ⁴ (W m ⁻²)	Figures
		HC (ppb)	HC/NO _x (ppbC/ppb)	Seed ¹	Seed mass ² (μg m ⁻³)						
Isoprene (C ₅ H ₈)											
IS01	10/04/2021	750	-	-	5	295-302	44-81	27	-	Fig. 2 (a)	
IS02	10/07/2021	782	13.3	-	5	297-301	42-56	31	-	Fig. 2 (b)	

IS03	10/20/2021	750	3.9	-		5		292-298	36-75	30	-	Fig. 2 (c)
IS04	12/16/2021	696	5.6	-		5		291-310	16-38	116	25.11	Fig. 3 (a)
IS05	01/27/2015	839	17.4	-		3		279-298	27-66	62	25.81	Fig. 3 (d)
α -pinene (C ₁₀ H ₁₆)												
AP01	03/19/2021	84	-	-		4		282-306	42-95	157	-	Fig. 2 (d)
AP02	06/23/2021	92	-	SA	100	4	0.72	296-899	72-88	96	-	Fig. 2 (g)
AP03	06/23/2021	79	-	wAS	100	4	0.33	296-300	89-100	80	-	Fig. 2 (g)
AP04	09/09/2021	64	10.5	-		5		296-299	34-42	37	-	Fig. 2 (e)
AP05	09/09/2021	58	10.5	SA	85	5	0.9-0.85	297-299	41-72	27	-	Fig. 2 (e)
AP06	09/20/2021	61	3.7	-		6		297-301	37-55	28	-	Fig. 2 (f)
AP07	09/20/2021	59	4.1	SA	87	6	0.85-0.75	298-302	37-55	33	-	Fig. 2 (f)
AP08	11/04/2021	60	2.3	dAS	40	5	0.33	288-294	32-45	58	-	Fig. 2 (h)
AP09	11/04/2021	60	2.3	-		5		289-293	44-66	63	-	Fig. 2 (h)
AP10	08/28/2019	124	11.3	-		4		296-320	14-40	23	36.21	Fig. 3 (b)
AP11	08/28/2019	130	10.7	SA	50	4	0.80-0.43	296-317	32-54	98	36.21	Fig. 3 (b)
AP12	07/18/2019	142	4.9	SA	60	3	0.85-0.47	294-320	13-42	52	37.34	Fig. 3 (e)
AP13	07/18/2019	139	4.6	-		3		294-319	19-48	28	37.34	Fig. 3 (e)
β -caryophyllene (C ₁₅ H ₂₄)												
BC01	11/10/2021	50				4		292-299	29-67	95	-	Fig. 2 (i)
BC02	11/10/2021	50		SA	70	4	0.72	293-298	36-72	73	-	Fig. 2 (i)
BC03	11/23/2021	40	4.2			3		278-293	40-72	65	-	Fig. 2 (j)
BC04	12/03/2021	50	10.5	SA	120	3	0.7-0.34	281-308	23-90	219	24.44	Fig. 3 (c)
BC05	12/03/2021	50	10.5			4		282-308	30-95	256	24.44	Fig. 3 (c)
BC06	12/10/2021	50	3.8			3		287-310	25-77	100	22.81	Fig. 3 (f)
BC07	12/10/2021	50	3.8	SA	150	3	0.78-0.42	288-311	26-72	87	22.81	Fig. 3 (f)

¹NS, SA, wAS, and dAS indicate non-seeded, sulfuric acid seed, wet ammonium sulfate seed, and dry ammonium sulfate seed, respectively. ²The seed mass is determined as a dry mass, without water mass. ³The pre-existing organic matter (OM₀) is determined for the chamber air prior to the injection of inorganic seed and HC. ⁴Maximum sunlight intensity is shown during the experiment measured by using the TUVR. For nighttime, the experiment was performed under the darkness without the sunlight.

28. 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.

Response: To present the aerosol acidity of each experiment, measured FS (fraction of sulfate = SO₄²⁻/(SO₄²⁻+NH₄⁺) ranges during the experiment has been added to the Table 1 as shown above.

29. 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.

Response: For the chamber study, sulfuric acid and ammonium sulfate have been used to demonstrate the neutral seed effect and the acidity effects on SOA formation. However, in the real

world, ammonium bisulfate could be the better inorganic seed to represent the ambient air. Thus, to implicate our model result to the real world, we simulate the ammonium bisulfate. To clarify this point, the manuscript has been revised by adding the sentence at P7 L243.

“To simulate the impact of aerosol acidity, the SOA formation is simulated in the presence of AHS seed, which is often found in ambient air. The reported acidity of the ambient aerosol is in the range of pH:-1~5 (Pye et al., 2020).”

30. P4 L124: Again, explicit to which degree? Which mechanisms were used (reference)?

Response: In this paragraph, the overall structure of the model was described. The detailed information of the explicit model and the further process of parameterization process is described in Sect. 3.1.

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

Response: The sentence has been removed from the revised manuscript. The detailed information about the explicit mechanism has been given in the Sect. 3.1.

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

Response: In this study, the salted aqueous solution includes only sulfate containing inorganics, such as sulfuric acid (SA), ammonium bisulfate (AHS), and ammonium sulfate (AS). The manuscript has been revised based on this comment.

L125: “For α -pinene and β -caryophyllene, the SOA formation in the presence of salted aqueous solutions (i.e., sulfuric acid (SA), ammonium bisulfate (AHS), and ammonium sulfate (AS)) was simulated under the assumption of the liquid-liquid phase separation (LLPS) between the organic and inorganic phase.”

33. 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.

Response: Isoprene SOA has high O:C ratio, indicating the high polarity, compared to other SOAs. Thus, several studies reported that the single homogenous mixed phase of the isoprene SOA in the presence of the inorganic seed. Thus, we conclude that there is a limitation to simulate isoprene SOA formation with our UNIPAR model due to the model assumption with LLPS. The manuscript has been revised to include this information in L128.

L128: “In case of isoprene, the production of single homogeneous mixed phase SOA has been reported in the presence of inorganic seed (Beardsley and Jang, 2016;Carlton et al., 2009). Thus, the isoprene SOA formation in the presence of inorganic aerosol was excluded.”

34. P4 L147: What do you mean by “was included to fulfill the oxidation mechanism in the current regional model”?

Response: The oxidation process of biogenic HC by O(³P) is generally insignificant path to produce SOA. However, in the regional scale model, biogenic HCs react with four major oxidants (OH radicals, O₃, NO₃ radicals, and O(³P)). To synchronize with the regional scale model, the oxidation path of biogenic HCs with O(³P) has been added. The manuscript has been revised.

L140: “Furthermore, the oxidation process of biogenic HCs by O(3P) (Paulson et al., 1992; Alvarado et al., 1998) was included to synchronize with the oxidation mechanism in the current regional model.”

35. P4 L157: “ α_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 “ α_i ”? Are these the elements of the unified array calculated for each hydrocarbon oxidation pathway? Please elaborate!

Response: α_i is the stoichiometric coefficient of gas product (i) and it was defined in L124 and L133.

L124: “The HC consumption obtained from gas mechanisms, stoichiometric coefficient (α_i), and physicochemical parameters of lumping species (i) were then applied to produce SOA mass (OM_T) via gas–particle partitioning (OM_P) and heterogeneous reactions (OM_{AR}) in both organic and inorganic phases.”

L133: “The UNIPAR model utilizes the stoichiometric coefficient (α_i) array and physicochemical parameters ($p_{L,i}^\circ$, MW_i , $O:C_i$, and HB_i) of the lumping species (i), which are determined by the explicitly predicted gas products.”

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

Response: OM_T is total organic matter, and it was defined in L124.

L124: “The HC consumption obtained from gas mechanisms, stoichiometric coefficient (α_i), and physicochemical parameters of lumping species (i) were then applied to produce SOA mass (OM_T) via gas–particle partitioning (OM_P) and heterogeneous reactions (OM_{AR}) in both organic and inorganic phases.”

37. P5 L 171: “... is also calculated as the traditional ...” should be “... according to the ...” or similar.

Response: The manuscript has been revised based on this comment.

“The partitioning coefficient of *i* into the inorganic phase ($K_{in,i}$, m³ μg⁻¹) is also calculated according to the absorptive partitioning theory:”

38. 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.

Response: To reduce the repetitions in the manuscript, the sentence has been rephrased as below:

“RO₂ and HO₂ concentrations, and the consumptions of biogenic HCs are predicted with SAPRC07TC for four different oxidation pathways, and they are applied to predict the gas phase concentration of lumping species and SOA formation in UNIPAR.”

39. 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”?

Response: Due to the hydrolysis of N₂O₅, the impact of inorganic seed on the nocturnal SOA formation was insignificant in the presence of NO_x. The manuscript has been revised based on this comment.

L223: “However, the impact of inorganic seed on nocturnal SOA formation can be insignificant in the presence of NO_x because N₂O₅ undergoes heterogeneous hydrolysis reaction on the surface of wet aerosol particles to form nitric acid (HNO₃) (Brown et al., 2006;Hu and Abbatt, 1997;Galib and Limmer, 2021).”

40. 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?

Response: The physicochemical properties of gas products were not measured. The oxygenated products and their physicochemical properties were predicted from the explicit gas mechanism. The solubility of the gas products has been considered in the model with the O:C ratio, hydrogen bonding, and molecular weight based on the gas simulation results. Based on our simulation, the impact of acidic seed on β-caryophyllene SOA formation appeared but it was small due to their poor solubility. This sentence has been relocated in L296.

L296: “The large molecules originating from β-caryophyllene oxidation might have a poor solubility in aqueous phase, weakening the impact of aerosol acidity on OM_{AR}.”

41. 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?

Response: This sentence has been removed in the revised manuscript. Please find the response for the referee's comment #33.

42. 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.

Response: Based on this comment, “But the reaction with O₃ is a minor.” has been removed from the revised manuscript.

43. 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).

Response: The additional discussion has been added in the revised manuscript based on the comment.

“ α -Pinene SOA yields are high with ozonolysis and NO_3 -initiated oxidation in both daytime and nighttime. Low volatile products form from the autoxidation of ozonolysis products as reported in the previous studies (Roldin et al., 2019; Crouse et al., 2013; Bianchi et al., 2019). The addition of NO_3 to the alkene double bond of α -pinene is followed by the addition of an oxygen molecule to form an alkylperoxy radical that can also lead to low-volatile peroxide accretion products (ROOR) (Hasan et al., 2021; Bates et al., 2022). The α -pinene ozonolysis SOA yield is insensitive to humidity even in the presence of hygroscopic, acidic AHS seed. Unlike isoprene SOA (Beardsley and Jang, 2016) or aromatic SOA (Han and Jang, 2022; Im et al., 2014; Zhou et al., 2019), α -pinene gas products are relatively hydrophobic and thus, less soluble in the aqueous phase.”

44. 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!)?

Response: The oxidation product from the β -caryophyllene is determined by simulating the explicit mechanisms and their physicochemical parameters were compared with that from other biogenic HCs. Based on the comment, the manuscript has been revised by adding the examples of the molecular weight of oxygenated products in reactive groups from three biogenic HCs.

L259: “In case of β -caryophyllene, even after the photodegradation the product volatility is still low enough to significantly partition to the aerosol phase and heterogeneously form SOA. Evidently, the molecular weight of β -caryophyllene oxidation products with high reactivity is generally higher than that in isoprene or α -pinene products. For example, the averaged molecular weight of β -caryophyllene oxidation products in highly reactive groups (VF or F) is $183.01 \text{ g mol}^{-1}$, while that from isoprene and α -pinene is $116.65 \text{ g mol}^{-1}$ and $143.29 \text{ g mol}^{-1}$, respectively.”

45. P8 L279: Throughout the document you often equate NO_x with the NO_3 radical, which can be done in parts at nighttime in the presence of ozone. However, during daytime jNO_2 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.

Response: In this section, SOA yields are simulated under the constrained oxidation path with a fixed amount of HC consumption to investigate the impact of product distributions of each oxidation path on SOA growth in day and night. Thus, this sentence describes the impact of NO_x levels on the oxygenated product from each oxidation path in day and night. For the clear understanding of readers, the purpose of this section has been added in L237 of the revised manuscript.

L237: “The atmospheric process of biogenic HCs is complex because of their multi-generation oxidations by the combination of various oxidation paths. To investigate the impact of product

distributions of each oxidation path on SOA growth in day and night, SOA yields are simulated under the constrained oxidation path with a fixed amount of HC consumption as seen in Fig. 4.”

46. 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!

Response: Yes, the manuscript has been revised.

L293: “The simulation of SOA yields in Fig. 4 is performed with the model parameters obtained in the presence of the wall effects.”

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

Response: The impact of gas-wall deposition is more under the non-seeded conditions than that in the presence of the inorganic seeds. Thus, by correcting the wall loss, the increase of SOA mass is more in the absence of inorganic seed than that with inorganic seeds, resulting the less difference in SOA mass between the non-seeded and seeded conditions. The sentence has been added in L299 of the revised manuscript.

L299: “The impact of the chamber wall on SOA formation in the presence of inorganic seed was less than that without the wet inorganic seed (Krechmer et al., 2020; Han and Jang, 2022).”

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

Response: For the chamber study, hydrocarbon and NO_x concentrations are overall high due to the experimental limitations. Firstly, for the chamber study there are gas-wall loss and particle-wall loss which can influence on the experimental data. With those losses, high concentrations of hydrocarbons need to be injected to get enough mass which is above the detection limit or instrumental uncertainties. To have various NO_x conditions, the target NO_x concentrations were determined based on the HC/NO_x ratio and needed HC concentration, resulting in the high concentration of NO_x in the chamber. To indicate the influence of the initial concentration of biogenic HCs and NO_x, the sensitivity of SOA model prediction to the initial HC concentration has been tested with three biogenic HCs and added to the SI.

49. 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?

Response: The temperature sensitivity has been shown in the Fig. 5. Figures S2 illustrates the contribution of each oxidation path to the HC consumption to support Fig. 5. To avoid the confusion, those explanations moved to the early in the same paragraph (L308).

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

Response: The oxidation of biogenic HCs is associated with various oxidation paths. In Sect. 4.2, To investigate the impact of product distributions of each oxidation path on SOA growth in day and night,

SOA yields are simulated under the constrained oxidation path with a fixed amount of HC consumption. However, in Sect. 4.3, all four oxidation paths contribute to the biogenic SOA formation with different contributions for various environmental conditions. Thus, both section 4.2 and Sect. 4.3 have been modified to better understand for the reader.

51. 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.

Response: The sentence has been removed in the revised manuscript.

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

Response: This part is to describe the simulation condition used for the sensitivity test and thus, this part is needed. To reduce the repetition, the sentence has been updated in revised manuscript as below:

“The simulations are performed in the absence of the gas-wall partitioning (Han and Jang, 2022) with the same given initial concentration of isoprene, α -pinene, and β -caryophyllene with Fig. 5.”

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

Response: “high NO_x zone” has been replaced with “high NO_x condition” in the revised manuscript as below:

54. 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?

Response: US commercial gasoline fuel (octane number: 87) was used. Its composition has been reported previously (Han and Jang, 2022). Around 30% of gasoline fuel were aromatic compounds.

Both α -pinene and gasoline fuel were introduced to the chamber in the form of gas (Section 2). Both α -pinene and gasoline concentrations were higher than those in ambient air. As discussed in the response to question 24 from reviewer 1, the concentrations of chamber experiments are limited by detection of instruments. For our chamber studies, gasoline total carbon concentrations were nearly 3000 ppbC and those of α -pinene were about 800 ppbC (80 ppb). In the urban area, the emissions are dominated by anthropogenic sources.

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

Response: The oxidation of aromatic hydrocarbons in gasoline fuel has been implemented by using the SAPRC07TC. The resulting HC (α -pinene and aromatic HCs) consumption, RO₂ concentration, and HO₂ concentration were applied to calculate the SOA formation with the SOA model parameters

from this study and Han and Jang, (2022). Thus, the SOA formation from the gasoline vapor has been counted in this study.

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

Response: Yes, aromatic compounds have been known to be a OH scavengers. Aromatic compounds in the gasoline fuel also could be a SOA source. In this study, the goal of this section is to investigate the nocturnal SOA formation of α -pinene and the resulting SOA formation from the anthropogenic precursors.

57. P10 L381: 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.

Response: This section is about the model uncertainties associated with the model parameters. This section has been relocated to the section 4.3 with the sensitivity test.

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

Response: The uncertainty test has been redone under the same relative humidity (RH =50%) with the sensitivity test.

59. P11 L394: Maybe “Conclusions” would be more fitting to this section!

Response: “Atmospheric Implications” is replaced with “Conclusions” in the revised manuscript.

60. P11 L411: “... under high NO_x zones ...” should be “concentrations” or “levels”.

Response: “high NO_x zones: has been replaced with “high NO_x levels” in the revised manuscript.

61. P11 L412: “Under the rural environment” should be “In rural environments” or “In a rural environment”.

Response: “Under the rural environment” has been replaced with “In rural environments” in the revised manuscript.

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

Response: Based on the comment, “Electrolytic inorganic salts” has been replaced with “Inorganic salts” in the revised manuscript.

63. P11 L419: “In this study ... showed a weak seed impact ...” How is this related to the previous statement about acidic seeds in other studies? Rephrase!

Response: The manuscript has been revised based on the comment as below:

“However, nighttime ozonolysis biogenic SOA in this study was insignificantly influenced by seed conditions as seen in the model simulation and chamber observations (Fig. 4).”

64. P11 L428: “... showing the higher biogenic HC emission” should be “showing higher biogenic HC emission(s)”.

Response: The manuscript has been revised based on the comment as below:

“There is a diurnal pattern in the biogenic HC emission showing higher biogenic HC emissions during daytime (Holzke et al., 2006;Chen et al., 2020;Petron et al., 2001;Goldstein et al., 1998).”

65. 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!

Response: The manuscript has been revised based on the comment as below:

“The concentrations of O₃ and NO₂ are generally high in ambient air at daytime, involving the photochemical cycle of NO_x in the presence of hydrocarbons.”

66. 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.

Response: The manuscript has been revised based on the comment as below:

“The model uncertainties to predict SOA mass mainly originates from the simplified gas mechanisms and the missing aerosol phase reactions.”

67. P12 L440: “Neither ... nor ... were not fully considered” In this context a double negation does not affirm but resolves to a positive. Rephrase!

Response: The manuscript has been revised based on the comment as below:

“Either complex cross reactions between RO₂ radicals or the long-term aging process of multiple generation products were not fully considered, which can be a source of the bias in SOA prediction.”

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

Response: The last paragraph of the manuscript has been revised to provide better flow and the conclusion and reads now,

“There are model uncertainties to predict SOA due to the simplified gas mechanisms and the missing aerosol phase reactions, although the UNIPAR model utilizes products originating from explicit gas mechanisms. For example, the daytime β -caryophyllene SOA of this study was underpredicted as seen in Fig. 3, suggesting that the improvement of explicit gas mechanisms is essential to better predict SOA formation. In the model, the multiphase reaction of biogenic HC is individually treated with four different oxidation paths. Either complex cross reactions between RO₂ radicals or the long-

term aging process of multiple generation products were not fully considered, causing a bias in SOA prediction. In the presence of inorganic seed, heterogeneous hydrolysis of N_2O_5 was assumed to be very rapid. However, the variation of aerosol constituents can influence the accommodation coefficient of N_2O_5 . For example, the heterogeneous hydrolysis of N_2O_5 on organic-coated aerosol can be slower than that in salted aqueous phase (Anttila et al., 2006). In addition, aerosol phase reactions such as hydrolysis of organonitrates and the oxidation of particulate OM were not included in the model. In the future, the performance of the UNIPAR model for the diurnal variation in biogenic SOA formation needs to be evaluated in regional scales (Yu et al., 2022).”

69. 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 NO_x to be a low NO_x case!

Response:

For the chamber study, hydrocarbon and NO_x concentrations are overall high due to the experimental limitations. Firstly, for the chamber study there are gas-wall loss and particle-wall loss which can influence on the experimental data. With those losses, high concentrations of hydrocarbons need to be injected to get enough mass which is above the detection limit or instrumental uncertainties. To have various NO_x conditions, the target NO_x concentrations were determined based on the HC/NO_x ratio and needed HC concentration, resulting in the high concentration of NO_x in the chamber. To indicate the influence of the initial concentration of biogenic HCs and NO_x, the sensitivity of SOA model prediction to the initial HC concentration has been tested with three biogenic HCs and added to the Sec. S5.

70. 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).

Response: The unit for the hydrocarbon concentration was wrong in the Table 1. Table 1 has been revised. Please find the revised table in the response of the comment# 27.

71. 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

Response: The caption has been revised based on the comment. the dotted line is OM_P.

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

Response: The SOA formation from the oxidation of biogenic HCs with O(³P) is insignificant in this simulation. In Fig. 4, SOA yield from O(³P) oxidation path is not visible.

73. 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.

Response: Figure 5 has been revised with large size of the graph and the scale of the Fig. 5(a) has been updated based on this comment.

74. 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.

Response: The reference sunlight intensity has been used for the sensitivity (Figs. 5 and 6) and uncertainty (Fig. S5) tests. The reference sunlight intensity measured on 06/19/2015 near summer solstice in the UF-APHOR illustrated in Fig. S1.

75. 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.

Response: Figure 6 has been updated based on the comment in the revised manuscript.

References

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- Krechmer, J. E., Day, D. A., and Jimenez, J. L.: Always Lost but Never Forgotten: Gas-Phase Wall Losses Are Important in All Teflon Environmental Chambers, *Environmental Science & Technology*, 54, 12890-12897, 2020.