Manuscript #: egusphere-2023-93

Response to Anonymous Referee #2

We would like to thank the reviewer for the time and the constructive comments on our work. The comments are reproduced below along with the author response. The changes made to the manuscript or supporting information were in red color.

Comment 1
In the introduction reference is made to "the SOA model" and I'm an unclear if this referring to a particular model or the more general idea of modelling SOA. This might be a case of just refining the language.
Response: The word "the SOA model" in Section 1 has been replaced by "SOA models".

Comment 2
"Volatility-reactivity based lumping species originating from explicit gas mechanisms allow to estimate their physicochemical parameters that process multiphase partitioning and in-particle reactions (i.e., oligomerization and acid catalyzed reactions)." I'm not sure I fully understand this sentence. Do you mean that by adopting an approach where species from a gas phase chemical mechanism are lumped based on their volatility and reactivity allows their physicochemical parameters, which are highly influential for the partitioning to multiphase aerosol and the subsequent in-particle reactions to be estimated?
Response: To response to the reviewer, the sentence has been revised as below,

"Chemical species originating from explicit gas mechanisms were lumped based on volatility and reactivity in the aerosol phase. The physicochemical parameters of lumping species allow the UNIPAR model to process multiphase partitioning and in-particle reactions (i.e., oligomerization and acid catalyzed reactions)."

Comment 3
I don't understand the use of the word "emerging" in line 56 – please could you clarify?
Response: The word "emerging" has been removed.

Comment 4
I think it would be worth mentioning that uncertainty in emissions of primary OM and secondary OM precursors may also contribute to model biases.
Response: Please find Section "3.1 Simulation of organic matter" for the description of the uncertainty in primary OC simulation and observation. For the secondary SOA precursors, please find the last paragraph in Section "4 Atmospheric implication and uncertainties" in the revised manuscript.

Comment 5
In the final paragraph you mention the expansion of the CAMx–UNIPAR model to include alkane SOA and nighttime chemistry of biogenic HCs in this work. There are then further descriptions of other changes made to CAMx–UNIPAR in other studies. It is not clear if these changes are also included in the version of CAMx–UNIPAR used in this study or not. This needs to be clarified. It would also be helpful if the additions to specific to this study were described in more detail and listed in the SI.
Response: To clearly show the new additions in the CAMx-UNIPAR model of this study, the last paragraph of Section 1 has been revised as follows,

"In this study, the CAMx–UNIPAR model has been updated to include the SOA formation from long-chain alkanes and nighttime chemistry of biogenic HCs. Long-chain alkanes are regarded as essential precursors for SOA formation (Aumont et al., 2012; Madhu et al., 2022). Madhu et al. (2022) have recently added an autoxidation mechanism into alkane semi-explicit oxidation mechanisms, improving the predictability of alkane SOA using the UNIPAR model against their chamber study. The resulting alkane model parameters have been newly implemented into CAMx-UNIPAR. In addition, the UNIPAR model of this study has been expanded to simulate biogenic SOA based on three major oxidation paths (i.e., OH radicals, ozone and nitrate radicals) being capable of nighttime SOA formation that is dominated by oxidation with ozone and nitrate radicals (Han and Jang, 2023)."

Comment 6

"These physicochemical parameters are universalized for five major precursor groups in UNIPAR (Table 1)." What does this mean?

Response: The sentence has been revised to clearly explain what five major precursor groups are as follows,

"These physicochemical parameters are unified for five major precursor groups (aromatics, alkanes, terpene, sesquiterpene, and isoprene) as shown in Table 1."

Comment 7

Where are SOA precursor emissions coming from? You mention they are "SAPRC07-based" but I don't know what this means.

Response: The sentence has been revised and reads now,

"The emission data of HCs is speciated to use SAPRC07 gas mechanisms…."

Comment 8

Have the emissions been validated? A bias in these emissions could mean the SOA model is getting the right/wrong answers for the wrong reasons in some cases. Fig 3 suggests a low bias in SOA which might come in part from an emissions bias.

Response: The emission data used in this study are based on California ARB(Air Resources Board)'s regional inventories and their own estimates and emission monitoring data for local sources. The emission processing went through QA/QC procedures.

Comment 9

"The lumping species in the lowest volatility is treated as non-volatile OM in this study." I don't understand this sentence – do you mean that the lumped species with the lowest volatility is automatically treated as non-volatile OM and so irreversibly partitions into the aerosol phase?

Response: The additional description has been added into Section 2.1 in the revised manuscript and reads now,

"The lumping species in the lowest volatility group are involved in oligomerization with a high reaction rate constant used for glyoxal, regardless of lumping groups' reactivity scale. The species in the lowest volatility group, which are multifunctional and dominantly present in aerosol phase, easily react in aerosol phase via various unidentified reactions (esterification and oxidations) and form non-volatile species."

Comment 10

In terms of OMP and OMH, I am unclear which relates to volatility-driven partitioning, which relates to reactive uptake and which relates to the dissolution of gases in aqueous phase aerosol. Differentiating between these is a key part of this model and so more detail is needed here.

Response: In order to clearly describe the UNIPAR model, the description of OMP and OMH in Section 2.1 has been modified in the revised manuscript as follows,

"4) The concentration of lumping species is distributed into gas (C_g), organic (C_{or}), and inorganic phases (C_{in}) using partitioning coefficients estimated based on Pankow's absorptive partitioning model (Pankow, 1994) with vapor pressure, the estimated activity coefficients of lumping species in both the organic and inorganic phases (Zhou et al., 2019; Yu et al., 2021c; Han and Jang, 2022; Madhu et al., 2022; Han and Jang, 2023), and aerosol's average molecular weight in each phase.

5) Kinetic parameters, such as lumping species' reactivity scales and their basicity constants, to calculate aerosol phase reaction rate constants in the organic phase and inorganic phase are reported in Tables S4–S5, respectively. The kinetic parameters used in CAMx-UNIPAR are updated by removing the artifact from gas-wall partitioning (Han and Jang, 2020; Han and Jang, 2022)

6) Heterogeneously formed OM (OMH), which is produced via oligomerization in the organic phase and the inorganic phase, is treated as non-volatile OM. The impact of viscosity on aerosol growth is also considered by including the equation term as a function of the average molecular weight of OM and the O:C ratio (Han and Jang,

2022). Aqueous reactions in the presence of wet-inorganic aerosol are operated by acid-catalyzed reactions and organosulfate formation and are processed under broad ranges of aerosol acidity ([H+]) and relative humidity (RH) levels to form both dry and wet inorganic aerosols. The lumping species in the lowest volatility group are involved in oligomerization with a high reaction rate constant used for glyoxal, regardless of lumping groups' reactivity scale. The species in the lowest volatility group, which are multifunctional and dominantly present in aerosol phase, easily react in aerosol phase via various unidentified reactions (esterification and oxidations) and form non-volatile species.
7) The SOA mass in UNIPAR is estimated by gas-particle partitioning (OMP) and heterogeneous reactions (OMH) in both organic and inorganic phase. The SOA mass formed from partitioning (OMP) is estimated using the Newtonian method (Schell et al., 2001) based on a mass balance of organic compounds between the gas and particle phases governed by Raoult's law. OMH is considered as a pre-existing absorbing organic material for gas-particle partitioning (Cao and Jang, 2010; Im et al., 2014). The resulting OMP is updated by the addition of C_{in}."

Comment 11
Line 245 – suggest you replace "degradation" with "decrease"
Response: "degradation" has been replaced by "decrease".

Comment 12
Throughout this paragraph I would use "bias" in place of "deviation". For example, "The low bias of the predicted SOA is generally greater than the high bias of the POA, which drives the low bias of the total OM from the observations."
Response: "deviation" in Section 3.1 has been replaced by "bias"

Comment 13
"The underestimation of SOA mass can be attributed to missing precursor HCs and unidentified chemistry in the gas and aerosol phases. For example, the SOA model is currently missing phenols, branched and cyclic alkanes, and polyaromatic hydrocarbons (i.e., naphthalene)." I'm not clear this is true without an evaluation of the emissions of the precursor species.
Response: The parameters in UNIAPR are continuously updated with the better gas mechanisms and expanded to include missing hydrocarbons. To support this information, we added citations as follows,

"For example, the precursor HCs such as phenols (Bruns et al., 2016; Majdi et al., 2019; Choi and Jang, 2022), branched and cyclic alkanes (Chan et al., 2013; Gentner et al., 2017; Madhu et al., 2023), and polyaromatic hydrocarbons (i.e., naphthalene) (Riva et al., 2015; Wang et al., 2021) are currently missing in the UNIPAR model."

Comment 14
"The simulated SOA/POA ratios were relatively lower than those in the observed ratios, as discussed for the different deviations of the predicted POA and SOA from the observations." I'm not sure I understand the second clause here. Do you mean that the lower SOA/POA ratio from the model is in line with the general model high bias of POA and low bias of SOA?
Response: The sentence has been revised as follows,

"The simulated SOA/POA ratios were relatively lower than those in the observed ratios, which are calculated using decoupled SOA and POA with a POC/EC ratio (Sect. 2.4), suggesting that POA is overpredicted and SOA is underpredicted in the CAMx-UNIPAR simulations."

Comment 15
"A strong wind appeared in the northern area, decreasing the residence time of pollutants, which reduced secondary products of pollutants in this region." What time period are you discussing here? From Fig S3, I can see wind speeds at San Jose are persistently higher than for the other locations.
Response: Overall, winds in the northern area were strong. To clarify this, "during the simulation period (Table S7 and Fig. S4)" has been added as below,

"A strong wind appeared in the northern area during the simulation period (Table S7 and Fig. S4), decreasing the residence time of pollutants, which reduced secondary products of pollutants in this region."

Comment 16

I understand that you cannot do anything about the 3-day averaging of the observational data but I do think the resulting lower number of observation data points means extending these simulations for at least another month or two would be warranted.

Response: We agree with the reviewer. The simulation of the air quality in CA was the first case to demonstrate CAMx-UNIPAR to regional simulation in the USA domain. Due to the frequent occurrence of wildfire in California, we had no choice but to select a season (Jan-Feb), when wildfires were inactive in 2018. In the future, CAMx-UNIPAR will be evaluated in different regions and different time.

Comment 17

It would also be helpful to have a timeseries plot of emissions at each site in a similar format to the line plots of Fig 3.

Response: Timeseries plots of emissions at each site have been added in the revised SI (Fig. S9)

Comment 18

In Figure 2(b-h), you give units of moles or g per second. I think the units of emission should be moles or g per second per unit area (I admit the final column in (b) could stay as moles/s). While I understand that the magnitude of the emissions of the different species vary considerably such that it would not be sensible to have a single common colorbar range for c-h, could cleanly separated ticks (e.g. 0, 2, 4, 6, 8, 10) be used for each to make comparison easier?

Response: Fig. 2 has been updated with a larger font size and the unit at mole (or g) s^{-1} $grid^{-1}$.

Comment 19

Similarly for Fig 6, I would strongly encourage the authors to consider either a log scale for the colorbar or make it much clearer that the concentrations span 2 orders of magnitude.

Response: Fig. 6 has been updated with a larger font size.

Comment 20

"Additionally, the model includes the low volatility products originating from autoxidation of α-pinene ozonolysis products (Roldin et al., 2019; Crounse et al., 2013; Bianchi et al., 2019). The importance of autoxidation mechanisms on terpene SOA formation was in a recent study by Yu et al. (2021c) for the daytime chemistry (Yu et al., 2021c)." While it is very good that you are considering highly oxidized species from α-pinene, could you provide any information about the yields you are using or whether you are using the full Roldin scheme which is substantial. Furthermore, the reference to the paper by Yu et al (2021c) is vague – what did this paper show?

Response: Additional description has been added as below,

"The importance of autoxidation mechanisms on terpene SOA formation was demonstrated in a recent study by Yu et al. (2021c) for daytime chemistry. In their study, the peroxy radical autoxidation mechanism (PRAM) developed by Roldin et al. (2019) was included in UNIPAR to evaluate the impact of HOMs on terpene SOA formation. In the sensitivity test of SOA prediction associated with PRAM, α-pinene SOA mass increased by 15–35% in the presence of PRAM, suggesting that substantial impact of PRAM on the total SOA mass (Yu et al., 2021c)."

Comment 21

Unless I have misunderstood the difference between OMH and OMP, I would have thought that the alkane autoxidation products would be in the OMP category given their highly oxidized structure and low volatility – please could you clarify?

Response: Some autoxidation products from alkanes belong to the lowest volatility group and participate in heterogeneous reactions to form OMH. Other autooxidation products, which are classified into partitioning only or slow reactivity are involved in OMP. Please find the response to comment 10.

Comment 22

A better color scale is needed for O_3 in Fig S10 since most of the region is off the top end of the scale.

Response: Fig. S10 in the original manuscript has been changed to Fig. S11 in the revised manuscript with a different color scale for O_3.

Comment 23
I am surprised by the low yield of SOA from aromatics. Can you provide any more detail about why this is quite so low?
Response: The low contribution of aromatic SOA to the total SOA mass is related to emissions of precursor HCs. Alkane is a dominant in anthropogenic HC emission (Fig. 2). Please also see the response to comment 5 from reviewer 1.

Comment 24
Data Accessibility. In the interests of community modelling and FAIR principles, I would like to see the code and model data uploaded to a freely accessible repository such as Github or Zenodo.
Response: The code of the CAMx-UNIPAR model is available upon request in Github.
CAMx-UNIPAR ver. 1.1, which included aromatics and biogenic daytime, is available in GitHub. The updated CAMx-UNIPAR ver. 1.2 has been preparing to include various precursors including alkanes (linear and branched alkanes), updated aromatics, and day/night biogenics. The updated version will include more hydrocarbons than the simulation of this study.

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