

**Manuscript #: acp-2021-1002**

**Response to Anonymous Referee #RC2:**

“Yu et al., describe the impact of implementing a state-of-science module for the formation of secondary organic aerosol from traditional as well as "novel" pathways including multi-phase processes involving particles. They evaluate their model against ground observations taken during a recent field campaign over South Korea for the duration of 1 month.

The manuscript is well written and presents the main findings in a concise and understandable fashion. Conclusions are sound presented in a balanced manner, mostly considering the state of the science in the field at this time. My main points are (1) the need to also focus on the remainder of the lifecycle of organic matter in the atmosphere, (2) to make better use of the wealth of data generated during KORUS-AQ to evaluate the model, and (3) a broader evaluation of the model performance. I would recommend major revisions.”

Response: We appreciate the reviewer for the time and effort on this study. Additional discussion about the aerosol lifecycle and the model evaluation using the field data are added in the revised manuscript. A line-by-line response to the reviewer’s comment is listed as below.

**Main points:**

(1) Organic aerosol lifecycle

Concentrations of OA in the atmosphere are determined by its sources (emission, secondary production) as well as its sinks. The authors claim to do better firstly because their model represents more of the physics and chemistry that probably takes place in the atmosphere, and secondly because it evaluates better against observations. I concur with the former, but find the latter needs to be discussed (further) in the manuscript. A lot of work has shown that OA can photolysis, age, and deposit in ways most models do not consider, thereby changing its properties and lifetime. Why is being closer to observations now "better" with UNIPAR, maybe you are just compensating model deficiencies in other areas?

Response: We agree with the reviewer that there are uncertainties associated with aerosol aging in the model of this study. In the CAMx-UNIPAR simulation, the deposition of the OA originated SOA was treated based on the one size bin for the fine particulate matter. The UNIAPR model include the aging of gas products but needs an aerosol aging process due to OA aging in the future. The discussion about aerosol deposition can be found in the section 2.1. The discussion about OA aging and aerosol deposition has been added to the section 4 Atmospheric implications and uncertainties and reads now.

“In addition, the deposition of SOA was estimated with the one particle size bin. The different particle size can have different sink fluxes causing the uncertainty in the lifetime

of OM. The UNIPAR model is capable of predicting aging of gas products but currently has no feature for OM aging.”

## (2) KORUS-AQ campaign data

KORUS-AQ was also a large aircraft campaign, a treasure trove of observations is readily available (including OA data!) from several aircraft platforms. It would be almost negligent to not use this data to evaluate a 3D m model simulation and instead focus only on three ground stations. There is so much more to learn about OA model performance when looking "up in the sky"!

Response: Thank the reviewer for the important comments. In the future, we will utilize the aircraft data. Prior to the compare the simulation with aircraft data, the evaluation of the aircraft data based on emission sources need to be performed.

## (3) Model performance evaluation

The authors have provided quite some data to look at overall model performance, but I suggest completing this in the following areas: how well is NO<sub>x</sub> represented, what is the performance for temperature and humidity, and how well does the model represent the main SOA precursor levels (aromatics, terpenes and isoprene)? Again, see point 2, there is a wealth of data available!

Response: The NO<sub>x</sub> observations during the KOROS-AQ were not available in many sites. We can find NO<sub>x</sub> observation data only at the Olympic Supersite of the selected four sites of this study (Figure S4). The sites chosen in this study are at best in the availability of various data and timeline.

The temperature and humidity were produced from the WRF model and they accorded well with the filed measurements ( $R^2 = 0.9999$  for temperature and  $R^2=0.9688$  for relative humidity). This information can be found in the figure caption in Figures S5 and S6 and reads now:

“The temperature inputs from the WRF simulation accords well with the filed measurements ( $R^2 = 0.9999$ ).”

“The RH for the CAMx meteorological inputs from the WRF simulation accords well with the filed measurements ( $R^2 = 0.9688$ ).”

Specific comments:

15 ff "explicit" gas-phase chemistry?

Response: Corrected and reads now.

“The UNified Partitioning-Aerosol phase Reaction (UNIPAR) model utilizes the explicit gas mechanism to better predict SOA formation from multiphase reactions of hydrocarbons.”

37 why italic for "via"?

Response: Word “via” was not italicized now.

37 HC abbreviation, first mention, explain!

Response: This has been corrected in the 2<sup>nd</sup> paragraph in introduction.

48: The fact that SOA precursors can undergo multi-phase chemistry involving a liquid-phase implies they are hygroscopic, which leads to important questions regarding their fate in the atmosphere. E.g., is deposition accounted for correctly (see, e.g., Knote et al., 2015)? Also, given that at least during daytime, we are in a photochemically active environment, what about photolysis losses of oxidized volatile organic compounds (OVOCs) (e.g., Hodzic et al, 2015)?

Knote, C., Hodzic, A., and Jimenez, J. L.: The effect of dry and wet deposition of condensable vapors on secondary organic aerosols concentrations over the continental US, Atmos. Chem. Phys., 15, 1–18, <https://doi.org/10.5194/acp-15-1-2015>, 2015.

Hodzic, A., Kasibhatla, P. S., Jo, D. S., Cappa, C. D., Jimenez, J. L., Madronich, S., and Park, R. J.: Rethinking the global secondary organic aerosol (SOA) budget: stronger production, faster removal, shorter lifetime, Atmos. Chem. Phys., 16, 7917–7941, <https://doi.org/10.5194/acp-16-7917-2016>, 2016.

Response: In the regional scale model, the produced SOA sinks via the dry and the wet deposition. The UNIPAR model considers the dynamic oxidation of gas products under varying NO<sub>x</sub> levels. In addition, the lumping species also sink to aqueous droplets (i.e., cloud) in the model and lose via the dry deposition. We agree with the reviewer in that SOA can be decomposed due to photolysis under the sunlight. The discussion about OA aging and the aerosol deposition has been added to the section 4, Atmospheric implications and uncertainties, and reads now.

“In addition, the deposition of SOA was estimated with the one size bin for the fine particulate matter. The different particle size can have different sink flux causing the uncertainty in the aerosol lifecycle of OM. The UNIPAR model is capable of the prediction of gas products aging but currently has no feature for OM aging.”

49: citations are for box models, better suited in relation to this study are examples for the regional and global scale, e.g. Budisulistiorini et al., 2017 (IEPOX), Knote et al., 2015 (GLYOXAL) and Stadler et al., 2018 (IEPOX), Myriokefalitakis et al., 2008 (GLYOXAL), respectively

Sri Hapsari Budisulistiorini, Athanasios Nenes, Annmarie G. Carlton, Jason D. Surratt, V. Faye McNeill, and Havalala O. T. Pye *Environmental Science & Technology* 2017 51 (9), 5026-5034 DOI: 10.1021/acs.est.6b05750

Knote, C., Hodzic, A., Jimenez, J. L., Volkamer, R., Orlando, J. J., Baidar, S., Brioude, J., Fast, J., Gentner, D. R., Goldstein, A. H., Hayes, P. L., Knighton, W. B., Oetjen, H., Setyan, A., Stark, H., Thalman, R., Tyndall, G., Washenfelter, R., Waxman, E., and Zhang, Q.: Simulation of semi-explicit mechanisms of SOA formation from glyoxal in aerosol in a 3-D model, *Atmos. Chem. Phys.*, 14, 6213–6239, <https://doi.org/10.5194/acp-14-6213-2014>, 2014.

Stadtler, S., Kühn, T., Schröder, S., Taraborrelli, D., Schultz, M. G., and Kokkola, H.: Isoprene-derived secondary organic aerosol in the global aerosol–chemistry–climate model ECHAM6.3.0–HAM2.3–MOZ1.0, *Geosci. Model Dev.*, 11, 3235–3260, <https://doi.org/10.5194/gmd-11-3235-2018>, 2018.

Myriokefalitakis, S., Vrekoussis, M., Tsigaridis, K., Wittrock, F., Richter, A., Brühl, C., Volkamer, R., Burrows, J. P., and Kanakidou, M.: The influence of natural and anthropogenic secondary sources on the glyoxal global distribution, *Atmos. Chem. Phys.*, 8, 4965–4981, <https://doi.org/10.5194/acp-8-4965-2008>, 2008.

**Response:** In order to respond to the reviewer, several references have been added to the revised manuscript and reads now (the 2<sup>nd</sup> paragraph in introduction).

“Several chemical transport models account for the aqueous reactions of few explicit products (i.e., glyoxal and IEPOX (epoxy diols form isoprene products)) that potentially may significantly impact the SOA formation (Ervens et al., 2011; Sumner et al., 2014; Budisulistiorini et al., 2017; Knote et al., 2014).”

51: citation to prove this claim?

**Response:** The references have been added to the revised manuscript and reads now (the 2<sup>nd</sup> paragraph in introduction).

“In particular, the current model applied to regional scales suffers from a substantial negative bias under high humidity conditions (Heald et al., 2011; Pye et al., 2017; Li et al., 2020).”

52: which "conventional model", not true in this broad claim form!

**Response:** The sentence has been modified in the revised manuscript and reads now (the 2<sup>nd</sup> paragraph in the introduction).

“The SOA model, such as the partitioning-base two product model, has no feature for SOA formation via aqueous phase reactions of different oxygenated products formed from various HCs.”

56: all these citations are the reference for UNIPAR, or is there a single one that serves as reference? It needs to be made clear where UNIPAR is scientifically published.

Response: The sentence has been modified in the revised manuscript and reads now.

“The UNified Partitioning-Aerosol phase Reaction (UNIPAR) model was developed by Im et al. (2014) to predict SOA mass based on multiphase reactions of toluene and 1,3,5-trimethylbenzene, was developed. In the UNIPAR model, the products predicted using explicit gas mechanisms are lumped based on volatility and emerging chemistry in the aerosol phase. This UNIPAR model has been extended to various SOA originating from isoprene, terpenes, aromatics, and gasoline and demonstrated through the extensive photochemical outdoor smog chamber data (Beardsley and Jang, 2016; Cao and Jang, 2010; Zhou et al., 2019; Yu et al., 2021; Han and Jang, 2022).”

59: what is "arrayed" supposed to mean?

Response: Word “arrayed” has been changed to “estimated” (the 3<sup>rd</sup> paragraph in introduction).

“The model parameters linked to the thermodynamic properties and aerosol chemistry are also estimated according to the lumped species characteristics.”

62: CAMx needs to be introduced (regional scale model...) and cited!

Response: This sentence has been modified in the revised manuscript and reads now (the 4<sup>th</sup> paragraph in introduction).

“In this study, the UNIPAR model was incorporated with the CAMx model (comprehensive air quality model with extensions, v7.10) (Environ, 2020) to predict the SOA formation in the regional scale during the Korean-United States Air Quality (KORUS-AQ) campaign that took place between 10 May, 2016 and 10 June, 2016.”

75: SOAP is quite outdated - there should be more recent developments for CAMx that would better show the effect of UNIPAR over the \_current\_ state of science. See e.g. Jiang et al., 2021, for references.

Jiang, J., El Haddad, I., Aksoyoglu, S., Stefenelli, G., Bertrand, A., Marchand, N., Canonaco, F., Petit, J.-E., Favez, O., Gilardoni, S., Baltensperger, U., and Prévôt, A. S. H.: Influence of biomass burning vapor wall loss correction on modeling organic aerosols in Europe by CAMx v6.50, Geosci. Model Dev., 14, 1681–1697, <https://doi.org/10.5194/gmd-14-1681-2021>, 2021.

Response: Thank you for the suggestion. In the future, we will implement the updated modules and parameters. In this study, our focus is the demonstration of the importance of aqueous phase reactions of organic species to form SOA by using the UNIPAR model.

75: Also, how do comparable model systems fare during KORUS-AQ? There is a good overview by Park et al., 2021, on multi-model results that should provide insights into how the model used here fares compared to others.

Rokjin J. Park, Yujin J. Oak, Louisa K. Emmons, Cheol-Hee Kim, Gabriele G. Pfister, Gregory R. Carmichael, Pablo E. Saide, Seog-Yeon Cho, Soontae Kim, Jung-Hun Woo, James H. Crawford, Benjamin Gaubert, Hyo-Jung Lee, Shin-Young Park, Yu-Jin Jo, Meng Gao, Beiming Tang, Charles O. Stanier, Sung Soo Shin, Hyeon Yeong Park, Changan Bae, Eunhye Kim; Multi-model intercomparisons of air quality simulations for the KORUS-AQ campaign. *Elementa: Science of the Anthropocene* 21 January 2021; 9 (1): 00139. doi: <https://doi.org/10.1525/elementa.2021.00139>

Response: The focus of our study is to demonstrate the importance of multiphase partitioning of organic species and their aqueous reactions (151 lumping species) by using the UNIPAR model. In particular, the UNIPAR can estimate the activity coefficient of lumping species on aqueous phase allowing the impact of aerosol water mass on SOA formation. In addition, the simulation in this study was compared to the ground-based observations during KORUS-AQ campaign.

In order to respond to the reviewer, we discussed the recent model simulation of the organic aerosol in the regional scale in the second paragraph of introduction and in the last paragraph of Section 3.1

“Park et al. (2021) extensively evaluated the prediction of the organic aerosol produced during the KORUS-AQ campaign by using different air quality models, which were varying in chemistry mechanisms, aerosol thermodynamics, the types of SOA precursors, and the SOA schemes. In their study, the SOA formation was simulated with the SOAP, the 4 bin-base VBS or the 5-bin-base VBS modules. The predicted organic aerosol masses were, however, underestimated compared to observation data (HR-ToF-AMS) suggesting the limitation of the current SOA modules.”

“For organic matter, the average Normalized Mean Bias (NMB, %) between model predictions and observations at the four monitoring sites are -50% for CAMx-SOAP and -39% for CMAx-UNIPAR. A similar level of the NMB ( $\approx 46\%$ ) was reported in the previous simulation for the same campaign (Park et al., 2021)”

141 ff: are organic acids considered when calculating aerosol acidity? How good is your aerosol water content, as it is crucial for acidity calculations?

Response: The aerosol acidity and the aerosol water content both were estimated by using the ISORROPIA inorganic thermodynamic model. In general, many inorganic thermodynamic models use the ZSR relation to estimate water activity of the system that is directly related to predict aerosol water content (Stokes and Robinson, 1966; Zdanovskii, 1948). It is known that the estimation of water prediction is relatively accurate and similar between models. However, the calculation of the activity coefficient of the proton in the highly concentrated salted system are uncertain due to the lack of database and it is various

between models as discussed in the previous studies (Jang et al., 2020; Pye et al., 2020). During the KORUS-AQ campaign, inorganic acids were significantly titrated, and aerosol acidity was near neutral. Thus, the aerosol water mass mainly influenced aqueous phase reactions of organics and their partitioning to aqueous phase.

142: typo "ISORRIPIA"

Response: This has been corrected.

“In order to process SOA formation in the inorganic aqueous phase, the inorganic composition and aerosol acidity are predicted by using the inorganic thermodynamic model, ISORROPIA (Fountoukis and Nenes, 2007), and then incorporated into the UNIPAR model. For the ISORROPIA model, mutual deliquescence relative humidity (MDRH) is predicted.”

155: "MOZART", all caps

Response: This has been corrected.

“The boundary conditions were converted from the MOZART-4 global simulation results (<https://www.acom.ucar.edu/wrf-chem/mozart.shtml>) (Emmons et al., 2010).”

194: I would expect at least a short model evaluation for the main drivers of OA formation: meteorology (temperature, humidity, radiation), oxidants (O<sub>3</sub>, NO<sub>x</sub>) and precursors (aromatics, terpenes, isoprene). See also main concerns.

Response: Please find the response to the 3<sup>rd</sup> main comment above.

210ff: how well does your model capture the precursors you actually included? Measurements of aromatics, terpenes and isoprene should be available!

Response: As seen in Section 2.3.2, the emission of air pollutants was determined by using SMOKE from emission inventories originating from various sources (i.e., point sources, area sources, biogenic sources (MEGAN), automobiles non-mobile sources, etc). During the KORUS-AQ campaign, only few precursors were monitored (i.e., toluene). The predicted toluene was on average 94% of observed toluene.

356ff: “Furthermore, the UNIPAR model integrated with regional models enables better prediction of future SOA burdens under different scenarios of air pollutant emissions.” This statement is too broad to be supported by the analysis shown here - why are you better equipped represent future scenarios better? Because you seem to compare better to 3 ground stations in one geographical corner of the world for 1 month in one year? Because you represent processes better? Address!

Response: The sentence has been removed.

Figure S5: do model and measurements coincide (i.e., the model is perfect), or might there be a difference in modelled vs. measured temperature, leading to differences in the thermodynamic environment that should be discussed? Figure S6: same question as for S6!

Response: Temperature and humidity in the model were obtained from the WRF simulation results and they accorded well with the measurements ( $R^2=0.999$  for temperature and  $R^2=0.969$  for relative humidity). This information can be found in the figure captions in Figures S5 and S6 in the revised manuscript.

## Reference

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