Manuscript #: acp-2021-1002

Response to Anonymous Referee #2:

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

Comment #1: Regarding the OA lifecycle:

(1) Deposition of particulate OA: using one size bin to estimate deposition fluxes for all sizes is overly simplified and will introduce an error, as the authors correctly state now. Why authors choose to implement it in such a way is unclear to me, as it would not introduce considerable computational overhead to do this for all sizes.

Response: The CAMx regional model employs a static two-mode coarse/fine (CF) scheme for the particle mass distribution. As an option, the evolving multi-section size scheme (Carnegie Mellon University, CMU) can be used but its compatibility with other model components is limited. For example, the current CAMx allows to operate the CMU scheme with ISORROPIA and SOAP chemistry integrated with the CB05 gas mechanism, but its development is not available for other gas mechanisms (i.e., SAPRC) or SOA modules (VBS). To clarify the setup of the aerosol size bin, the sentence has been added to the section "2.3.1 Simulation domain and model configurations" in the revised manuscript and reads now.

"The two-mode coarse/fine (CF) scheme for the particle mass distribution was employed. In the CAMx, the multi-section size scheme can be operated with ISORROPIA and SOAP chemistry integrated with CB05 but it is currently not comparable with other gas mechanisms such as SAPRC or other SOA modules (i.e., VBS modules)."

(2) Deposition of gaseous OA (also known as condensable vapors): there has been quite some work on the influence of the wet and dry deposition of gaseous-phase OA components (condensable vapors) have also on particulate OA due to the fact that they are in thermodynamic equilibrium. How are condensable vapors deposited, what assumptions about Henrys law constants are made, and are they similar for SOAP and UNIPAR?

While you have somewhat answered my question in the authors response, none of the gas-phase deposition or photolysis language actually made it into the manuscript. You should revise your changes. I think these merits mentioning it also to the reader of manuscript if it is accepted.

Response: The deposition of aerosols and gas species in this study was estimated with the default module existing in the CAMx model and has no difference between SOAP and UNIPAR simulations.

As described in the CAMx User Guide v7.10 (Environ, 2020), the wet deposition model in the CAMx regional model employs a scavenging coefficient, which are determined differently for gases and particles. Briefly, the wet scavenging is calculated for each layer within the precipitating grid column from the top of the precipitation profile to the surface. The gases species dissolved in the precipitation water are in equilibrium with ambient air concentrations according to Henry's law constant, aqueous dissociation, cloud water temperature and acidity. In this study, the Henry's law constant of gas species used in the gas oxidation mechanism, SAPRC07TC, was preset in the parameter files of the CAMx regional model and used for both SOAP and UNIPAR simulations. For particles, the wet scavenging rate is dependent on the rainfall rate, the drop diameter, and the collection efficiency, which is a complex function of particle size, density, hydrometeor size, fall speed, kinematic viscosity of air and water. The dry deposition of gases compound and particles are estimated depending on a deposition velocity, which is function of solubility, diffusivity, density, particle size, the meteorology, and the surface characteristics.

To explain the aerosol and gas deposition process in CAMx, the following sentence has been added to the section "2.3.1 Simulation domain and model configurations" and reads now.

"The dry and wet depositions of aerosols and gas species were estimated with the module existing in the CAMx model for both SOAP and UNIPAR simulations. The detailed explanation for the deposition model can be found in the CAMx User Guide v7.10 (Environ, 2020)."

Comment #2: Regarding the aircraft data from KORUS-AQ:

I would strongly suggest to the authors to reconsider their stance on (not doing) a model evaluation against KORUS-AQ aircraft data. Organic aerosol, created from a multitude of sources and processes, constantly changing in the atmosphere, and existing in thermodynamic equilibrium between particle and gas-phase is such a complex system that special care needs to be taken to evaluate an equally complex model parameterization. Authors would be well advised to evaluate their model under as many diverse atmospheric conditions (concentration levels, distance from emission source, mixture types, temperatures, humidities) as they can get their hands on to get a robust understanding of the actual performance of their parameterization. Using only a few ground stations which are in principle prone to local processes not resolved by the model grid (strong emitters close by, special topography and wind systems, nocturnal boundary layer height ...) is not

enough. Authors could also not dispel my concerns regarding compensating errors from looking only towards OA formation instead of all processes in the OA lifecycle, which casts further doubt on evaluating only against a few ground stations.

And finally, I do not understand what authors meant to say by "Prior to the compare the simulation with aircraft data, the evaluation of the aircraft data based on emission sources need to be performed.". The aircraft data collected during KORUS-AQ has been quality controlled and evaluated multiple times in diverse contexts, see the KORUS-AQ overview paper (Crawford et al., 2021, https://doi.org/10.1525/elementa.2020.00163) and references therein.

Response: The aircraft data that are collected within several hours is different from ground-based data collected in a continuous mode. Aircraft data collection is also performed under the fast speed (several kilometers per minute) and its altitude ranges from several hundred meter to 7km (sometimes, higher than Planetary Boundary Layer (PBL)). Aircraft data is influenced by vertical convection and mixing of an air parcel. For understanding of aerosol compositions and chemical transformation, both aircraft data and ground-based observations are valuable. The flight tracks of NASA DC-8 aircraft missions during the simulated period of this study are shown in Figure S11 in the revised supporting information.
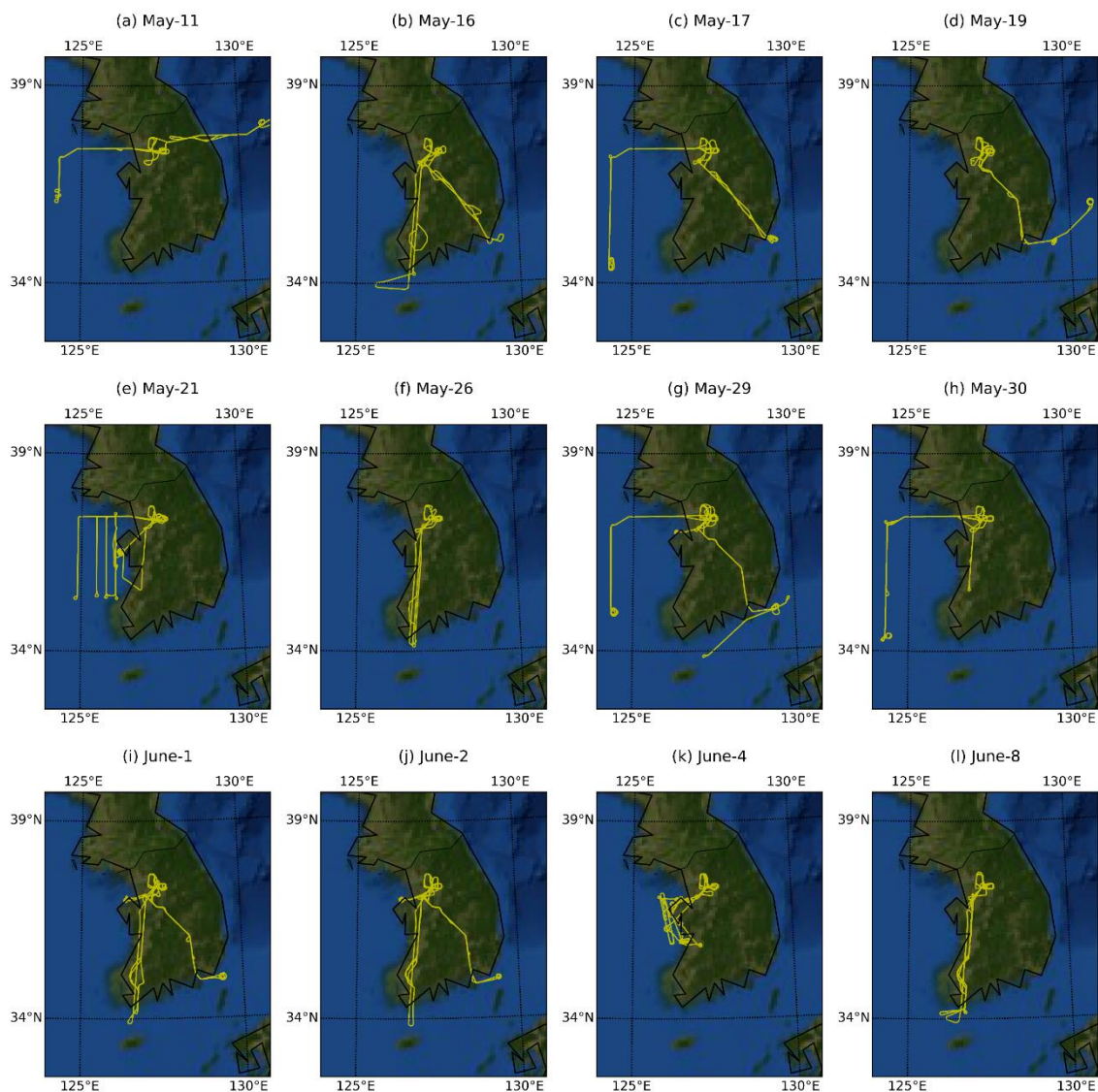
Figure S11. Flight tracks of NASA DC-8 aircraft missions during the simulated period and regions of this study.

We have reviewed the available data of NASA DC-8 aircraft mission during the KORUS-AQ campaign. The observed data for ozone, NO, NO_x, and toluene were available in 12 different flight missions (4-6 hours each) between May 10 and June 10 in 2016. The comparison of the observations and the model predictions for ozone, NO, NO_x, and toluene gas is plotted in Figure S11 in the revised supporting information. The AMS data collected from the aircraft during the DC-8 flight missions are Organic Carbon (OC) concentrations specifically in PM_1 and thus, they are not directly comparable to the simulated total organic matter. Figure S12 shows the correlation between AMS data and the simulated primary organic aerosol (POA) or the simulated secondary organic aerosol (SOA). A higher

correlation coefficient appears between AMS data and the simulated SOA (PCC = 0.57) than that between AMS data and the simulated POA (PCC = 0.38), indicating that the observed OC in the high altitude is much more influenced by secondary pollutants.

Following paragraph is added to the end of Section 2.4 "Observations during the KORUS-AQ campaign" in the revised manuscript and reads now.

"The KORUS-AQ campaign performed several flight measurements by using the NASA DC-8 research aircraft with a comprehensive payload for in situ sampling of trace gas and aerosol compositions. Fig. S11 shows the flight tracks of the NASA DC-8 aircraft missions during the KORUS-AQ campaign between May 10 and June 10 in 2016. The observed airborne concentrations of ozone, NO, NO_2, and toluene are plotted against the simulation from the CAMx-UNIPAR model (Fig. S12)."

(a) ozone

n = 92
mean_x = 86.33
mean_y = 66.54
PCC = 0.50
MBE = -19.79
NMB = -22.9%

(b) NO

n = 83
mean_x = 0.23
mean_y = 0.50
PCC = 0.54
MBE = 0.27
NMB = 119.5%

(c) NO2

n = 83
mean_x = 0.89
mean_y = 1.47
PCC = 0.64
MBE = 0.58
NMB = 64.6%

(d) toluene

n = 95
mean_x = 0.38
mean_y = 0.29
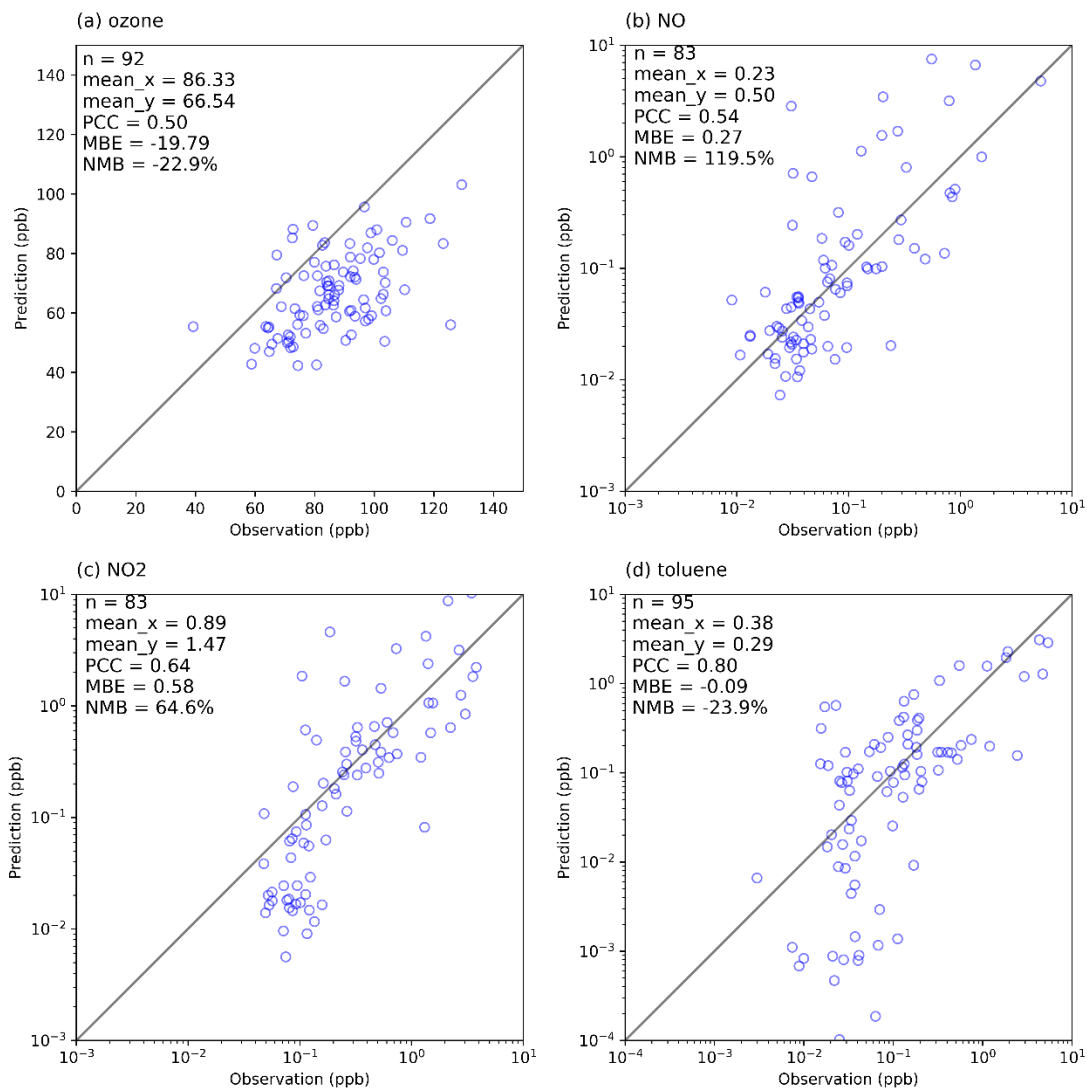PCC = 0.80
MBE = -0.09
NMB = -23.9%

Figure S12. The observations vs. the simulated concentration (ppb) of (a) ozone, (b) NO, (c) NO_2, and (d) toluene during the NASA DC-8 aircraft missions of the KORUS-AQ campaign. The CAMx-UNIPAR was used for the simulation output. Terms "MBE", "PCC", and "NMB" represent mean bias error, Pearson correlation coefficient, and normalized mean bias, respectively. The detailed equations for the statistic calculation are listed in Table S2. The grid size for CAMx-UNIPAR simulation was 9 km × 9 km. The data collection in on-board observation was performed every second. The on-board data was averaged for 30 seconds, which is equivalent to approximate 6 km distance (less than a grid width). The maximum aircraft ground speed was about 200 m/s.
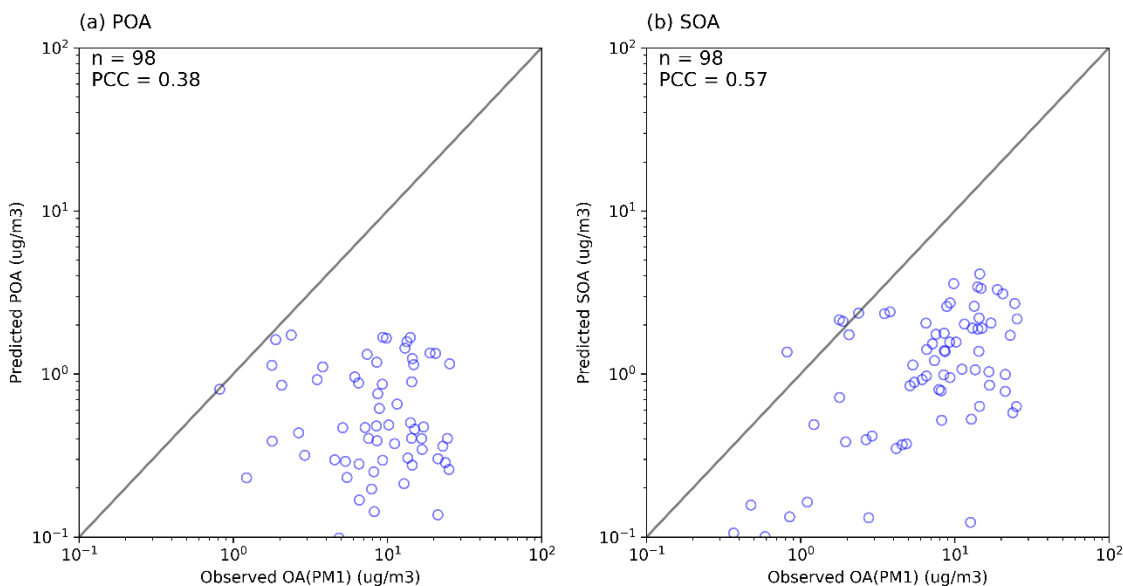

Figure S13. The correlation between the observed organic aerosol (OA) concentration (ug/m^3) and the predicted primary organic aerosol (POA) (a) or the predicted of SOA concentration (μg/m^3) (b). The observed OA data in PM_1 were measured by using Aerosol Mass Spectrometer (AMS). Term "PCC" is the Pearson correlation coefficient. The simulated SOA mass is the sum of the OM produced via gas-particle partitioning and heterogeneous reactions of organics by using the UNIPAR module.

The section for gas simulation was newly added to "3.4 Simulated concentrations of gaseous species" in the revised manuscript and reads now.

"3.4 Simulated concentrations of gaseous species

Fig. S10 illustrates the correlation between the 8-hour averaged observations and the 8-hour averaged predictions of ozone, NO_x, SO_2 and toluene at the Olympic Park supersite. In general, the model prediction slightly underestimates ozone (Fig. S10a), SO_2 (Fig. S10c), and toluene (Fig. S10d), but overestimates NO_x (Fig. S10b). Similarly, underestimation of ozone appeared in the on-board data (Fig. S12a). This underestimation

could be explained by the missing or the underestimation of ozone precursors (i.e., toluene as shown in Fig. S12d) in the current emission inventories.

Fig. S13 shows the correlation between Aerosol Mass Spectrometer (AMS) data and the simulated primary organic aerosol (POA) or the simulated secondary organic aerosol (SOA). A higher correlation coefficient appears between the AMS data collected during the DC-8 flight missions and the simulated SOA (PCC = 0.57) than that between AMS data and the simulated POA (PCC = 0.38), indicating that observed OC in the high altitude is more influenced by secondary pollutants."

Comment #3: Regarding model performance evaluation:

Authors did not reply to my comment on evaluating against main SOA precursors - this is crucial to understand whether their OA formation processes are accurate. Again - there is data readily available.

Authors state regarding temperature and RH evaluation: "The temperature inputs from the WRF simulation accords well with the filed

88 measurements (R2 = 0.9999)." and "The RH for the CAMx meteorological inputs from the WRF simulation accords well with the

94 filed measurements (R2 = 0.9688)." None of the plots in S5 or S6 show a line for observed values, and I find it difficult to believe they would match perfectly all the time, and a R2 (squared!) of 0.9999 is not believable. Also, it is unclear to me what "RH for the CAMx meteorological inputs from the WRF simulation" is supposed to mean. Finally, there is a typo in "filed" measurements.

Response: In the previous revision, the intercept in the statistic regression between the observations and the simulation for temperature and RH were set to zero, which resulted R^2 value as high as 0.99. When the intercept is included, the R^2 is 0.885 for temperature and 0.738 for relative humidity. The plots for the observations versus the model prediction from WRF are newly added to the Supporting information (Figure S8). The predicted temperature at the Olympic Park supersite has less bias (NMB=-0.002) from observations compare to RH (NMB=-0.03).
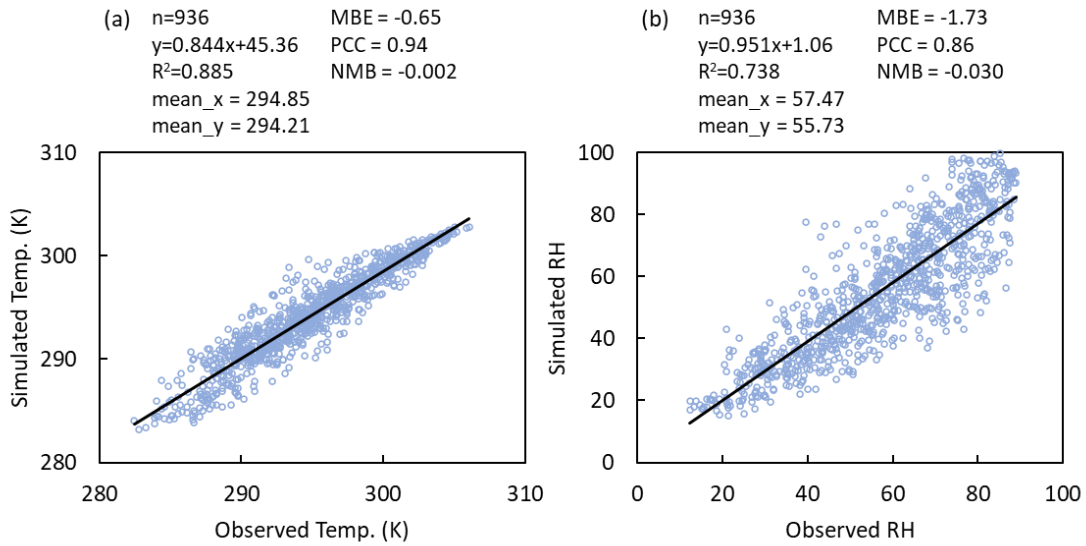
(a)
n=936	MBE = -0.65
y=0.844x+45.36	PCC = 0.94
R^2=0.885	NMB = -0.002
mean_x = 294.85	
mean_y = 294.21	

(b)
n=936	MBE = -1.73
y=0.951x+1.06	PCC = 0.86
R^2=0.738	NMB = -0.030
mean_x = 57.47	
mean_y = 55.73	

Figure S8. Observations versus WRF simulations for (a) temperature (K) and (b) relative humidity (RH) at the Olympic Park supersite. "MBE", "PCC", and "NMB" represent mean bias error, Pearson correlation coefficient, and normalized mean bias, respectively. The definitions for the statistic calculation are listed in Table S2.

To evaluate the model performance, the time profiles of the ground observations and simulation from CAMx-UNIPAR for toluene and benzene at the Olympic Park supersite are newly added to the supporting information (Figure S5). For isoprene, the observation was not available. The correlation between observations and simulations for ozone, NO_x SO_2, and toluene at the Olympic Park supersite are shown in Figure S10 in the supporting information.
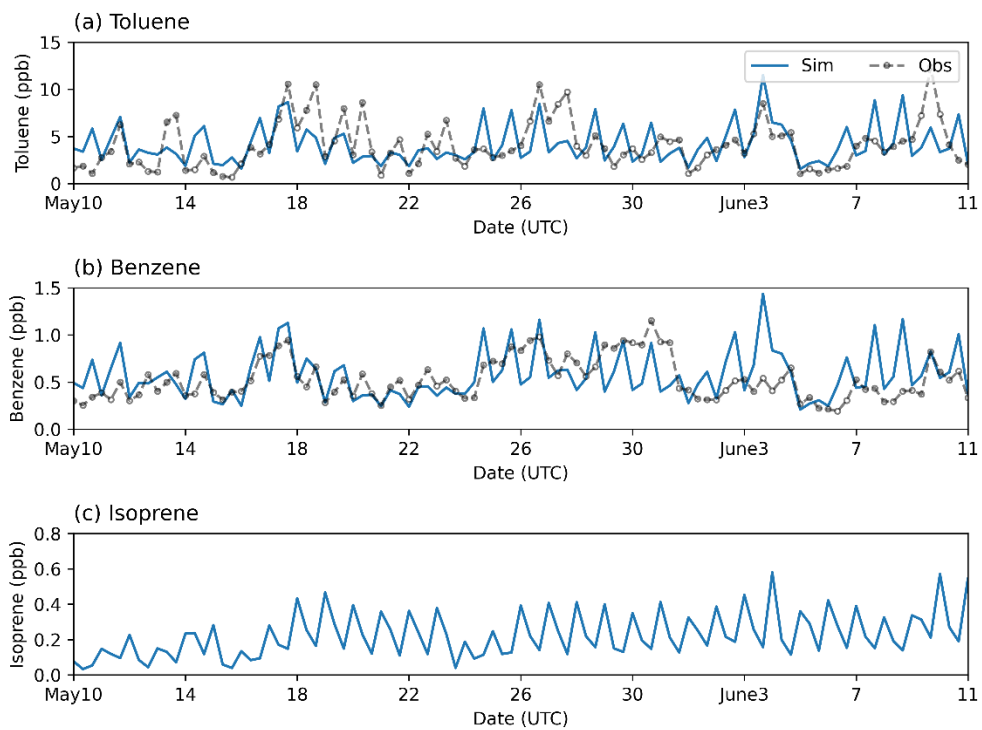
Figure S5. Time profiles of the observed and predicted concentrations of (a) 8-hour averaged toluene, (b) 8-hour averaged benzene, and (c) 8-hour averaged isoprene at the Olympic Park supersite. For isoprene, the observation was not available.
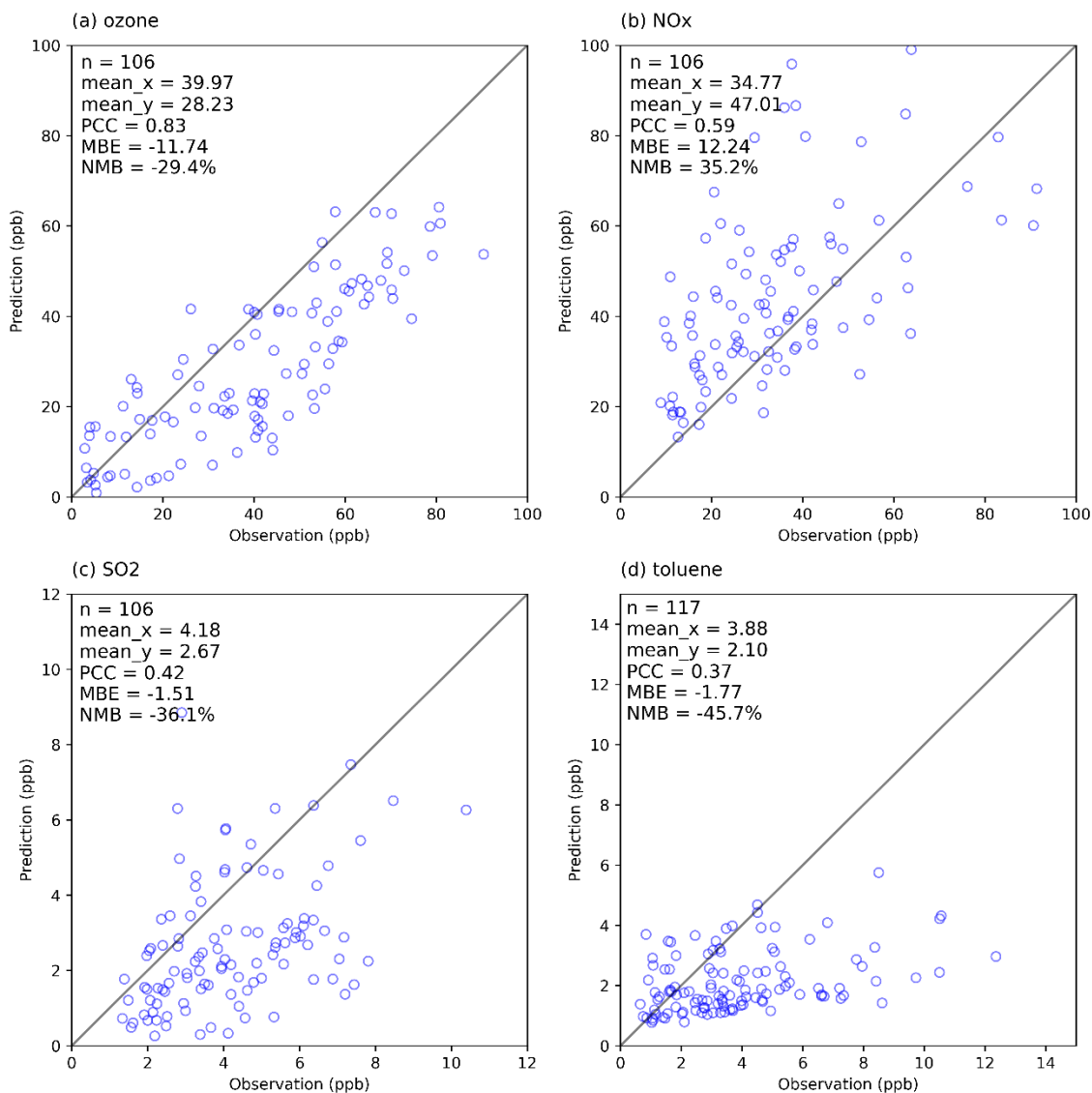
Figure S10. The 8-hour averaged observations vs. simulated concentration (ppb) of (a) ozone, (b) NO_x, (c) SO_2, and (d) toluene at the Olympic Park supersite. The CAMx-UNIPAR was used for the simulation output. Terms "MBE", "PCC", and "NMB" represent mean bias error, Pearson correlation coefficient, and normalized mean bias, respectively.

The following sentences are added to the end of section 2.4, "Observations during the KORUS-AQ campaign" of the revised manuscript and read now.

"In Fig. S5, the simulated concentration of SOA precursors, including toluene, benzene and isoprene, are plotted against the observations at the Olympic Park supersite. For isoprene, the observation was not available. For meteorological inputs, the observed temperature and RH at the Olympic Super site are plotted versus the simulations in Fig. S7.

Overall, the smaller bias between observations and predictions appeared in temperature compared to RH."

Comment #4: Regarding organic acids and acidity calculations:

Thank you for this concise elaboration - I would strongly suggest to actually put it into the manuscript, so other readers will also benefit!

Response: We thank the reviewer for the suggestion. The descriptions of the aerosol acidity and the aerosol water content have been added to Section S2 of the revised supporting information and read now.

Section S2: Prediction of aerosol inorganic composition and aerosol acidity

Both the aerosol inorganic composition and aerosol acidity are estimated by using the ISORROPIA inorganic thermodynamic model (Nenes et al., 1998; Fountoukis and Nenes, 2007). In general, many thermodynamic models, such as E-AIM (Clegg et al., 1998) and ISORROPIA (Nenes et al., 1998; Fountoukis and Nenes, 2007), employ the ZSR relation to estimate water activity of the system that is directly related to the prediction of 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 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, the inorganic acid was mostly titrated with ammonia gas as shown in Figure S1-S3, and aerosol was near neutral. Thus, the aerosol water mass mainly influenced aqueous phase reactions of organics and their partitioning to aqueous phase.

In order to accurately predict the aerosol phase status (liquid or solid phase), the prediction of deliquescence relative humidity (DRH, 0-1) and the efflorescence relative humidity (ERH, 0-1) are essential in this study. The mutual deliquescence relative humidity (MDRH) is predicted by using ISORROPIA model. In a multicomponent inorganic mixture, the MDRH is the RH that all salts are simultaneously saturated with respect to all components. ERH is predicted by using the neural network model based on inorganic composition (Yu et al., 2021) as following equations.

$$N_1 = 1.54463 \times f_{anion} - 0.9243 \times f_{nitrate} - 0.073745 \tag{S9}$$

$$N_2 = -0.63382 \times f_{anion} + 0.82856 \times f_{nitrate} + 0.288342 \tag{S10}$$

$$N_3 = -0.18594 \times f_{anion} + 0.63382 \times f_{nitrate} + 0.366726 \tag{S11}$$

$$N_i' = \begin{cases} N_i \geq 0, N_i \\ N_i < 0, 0 \end{cases} \quad i = 1,2,3 \tag{S12}$$

$$N_4 = -0.50581 \times N_1' - 1.15781 \times N_2' + 0.68805 \times N_3' + 0.33499 \qquad \text{(S13)}$$

$$N_4' = \begin{cases} N_4 \geq 0, N_4 \\ N_4 < 0, 0 \end{cases} \qquad \text{(S14)}$$

$$ERH = 2.21228 \times N_4' + 0.00018 \qquad \text{(S15)}$$

f_{anion} is the fraction of anion charges to total ion charges excluding proton and $f_{nitrate}$ is the mole fraction of nitrate to total anion. Series of N in equations denotes nodes in the neural network model.

Reference

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