Response to the reviewer1 (Manuscript Ref. NO.: acp-2021-649)

We would like to thank the reviewer for their time, and useful comments. Their comments are repeated below, followed by our response.

General comments:

Han and Jang provide some modeling insights on the photooxidative fates of gasoline emissions, using an SOA growth model with corrective terms that account for gas-wall partitioning phenomena that may bias kinetic inferences from experimental chamber data. Simulations across a range of NO_x and seed aerosol conditions were developed and compared to observations of ambiently irradiated aerosols in the University of Florida atmospheric chamber, showing reasonable consistency between estimated and measured SOA mass. Further, the authors report broad-strokes sensitivity analyses for a variety of initial conditions and model parameters.

While the core content of the authors' work is interesting and relevant to the field at large, some minor revisions focusing on the reworking of introduction and discussion would be necessary prior to its wider release. In particular, further explanation and disambiguation of certain experimental or modeling decisions would be helpful to better reinforce the authors' assertions in their analysis. Therefore, I recommend this manuscript for publication upon the resolution of the following questions and comments.

Specific Comments:

1. A major takeaway of this manuscript is that it is necessary and important to implement corrections for gas-wall partitioning into SOA models. While perhaps an obvious statement to make, I believe it would be useful to underscore that GWP is a largely unavoidable artifact of the experimental data that informs SOA models and is not based in ambient atmospheric phenomena. The authors note that GWP can vary through several different operational and experimental factors; providing illustrative ranges for wall-loss rate coefficients, similar to the Introduction section of Cappa et al. 2016 (Cappa et al., 2016) will help contextualize the magnitude of these contributions to overall mass balances to the reader.

   Response:

   The magnitude of GWP is closely related to the wall loss rate coefficient ($kon_{w,i}$ in this paper). The range of $kon_{w,i}$ and the impact of GWP on aromatic SOA are now given in the Section 4.1. Please see L245, L248, and L253 in the revised manuscript:

   L245: "The estimated absorption rate constant ($kon_{w,i}$) of i to the chamber wall was ~5×10^{-4} s^{-1} for UF-APHOR chamber, differed by the volatility and functionalities of the lumping structures."
   L248: "In case of high NO_x level, SOA mass from the photooxidation of benzene insignificantly increased as a factor of 1.04 after GWP correction, compared to other aromatic HCs which can produce 1.14-4.75 times higher SOA mass in the absence of GWP impact."
   L253: "The C_{SOA} to $C_{SOA,wall}$ ratio is higher under the NS condition (~4.75) than that in the presence of wAHS (~2.54)."

2. Overall: Given that there are many acronyms and abbreviations used throughout this manuscript, it may be helpful (though perhaps not necessary) to include a glossary or list of abbreviations in the SI to improve general readability.

Response:

The list of the abbreviation and acronyms have been added in SI as a Table S3 in the revised manuscript as below:

Table S3. The list of the acronyms and abbreviation in the manuscript and their definitions.

Acronyms or abbreviation	Definition
GWP	Gas-Wall Partitioning
HC	Hydrocarbon
QSAR	Quantitative Structure Activity Relationship
RH	Relative Humidity
OC	Organic carbon
ΔHC	The consumption of hydrocarbons
$[RO_2]$	The concentration of RO_2
$[HO_2]$	The concentration of HO_2
α_i	The stoichiometric coefficient of the lumping species *i*
OM_T	Total SOA mass
OM_P	The SOA mass generated via gas–particle partitioning
OM_{AR}	The SOA mass generated via heterogeneous reactions in organic and inorganic phases
$p_{L,i}^{\circ}$	Vapor pressure of the lumping species *i* (mmHg)
MW_i	Molecular weight of the lumping species *i* (g/mol)
$O{:}C_i$	Oxygen to carbon ratio of the lumping species *i*
HB_i	Hydrogen bonding of the lumping species *i*
R_i	Reactivity scale of the lumping species *i* in the aerosol phase
$C_{g,i}$	The gas concentration of lumping species *i*
$C_{or,i}$	The concentration of lumping species *i* partition onto the organic phase
$C_{in,i}$	The concentration of lumping species *i* partition onto the inorganic phase
$K_{or,i}$	The partitioning coefficient of *i* into the organic phase
$K_{in,i}$	The partitioning coefficient of *i* into the inorganic phase
MW_{or}	The averaged molecular weight of OM_T (g mol^{-1})
R	The ideal gas constant (8.314 J mol^{-1} K^{-1})
T	Temperature (K)
MW_{in}	The averaged molecular weight of inorganic aerosol (g mol^{-1})
$\gamma_{or,i}$	The activity coefficient of *i* in organic phase
$\gamma_{in,i}$	The activity coefficient of *i* in inorganic phase
FS	Fractional sulfate
SA	Sulfuric acid
AS	Ammonium sulfate
$C_{or,i}^{'}$	The concentration of *i* in the organic aerosol phase (mol L^{-1})
$C_{in,i}^{'}$	The concentration of *i* in the inorganic aerosol phase (mol L^{-1})
$k_{AC,i}$	The reaction rate constant in the aqueous phase
$k_{o,i}$	The reaction rate constant in the organic phase
$pK_{BH_i^+}$	The protonation equilibrium constant
X	The excess acidity
a_w	The water activity
$[H^+]$	The proton concentration
$C_{T,i}$	The total concentration of *i*
$C_{g,i}^{*}$	the effective saturation concentration of *i*
OM_0	The pre-existing OM concentration (mol m^{-3})
OM	The organic matter

$MW_{oli,i}$	The molecular weight of the dimer (g mol^{-1}).
kon_w	The absorption rate constant of *i* into the chamber wall
$koff_w$	The desorption rate constant of *i* from the chamber wall
LLPS	Liquid-liquid phase separation
NS	No-seeded
wAHS	Wet ammonium bisulfate
dAS	Dry ammonium sulfate
C_{SOA}	The aromatic SOA mass in the absence of GWP bias (μg m^{-3})
$C_{SOA,wall}$	The aromatic SOA mass in the presence of GWP bias (μg m^{-3})
ERH	Efflorescence relative humidity
DRH	Deliquescence relative humidity

3. Section 2 and Table 1: The information provided is likely enough to approximate or infer the duration and magnitude of sunlight that the University of Florida chamber is exposed to in each run. However, it may be helpful for the authors to provide rough estimations for the maximum actinic flux for each day so that the reader can more easily get a feel for the ranges of irradiance across experiments, much like how the ranges of temperatures and relative humidity values are presented. For instance, it is not immediately apparent that the approximate duration between dawn until dusk is 10 hours in January/December, which better justifies the experiment length mentioned on Line 84. The authors provide a reference sunlight intensity that is used in their models, though taken in the end of a Spring season instead of a Winter season. Do the authors expect differences in seasonal incident sunlight to contribute to any potential inconsistencies in results?

Response:
The intensity of sunlight, which is related to actinic flux changes with season and weather conditions (cloud coverage). During chamber experiments, TUVR is continuously measured (see section 2) and applied to photolysis of chemical species in gas mechanisms. The reference sunlight intensity was measured near summer solstice to cover a large aging scale. In springtime, hydrocarbon is less aged during the photooxidation of hydrocarbons than that in summer. To clarify the experimental condition, maximum sunlight intensity measured by TUVR has been added in the Table S1 in the revied manuscript.

Date (Chamber ID)	Initial condition					Temp (K)	%RH	max OM (µg m^{-3})	Max TUVR (W m^{-2})^e	Figure
	HC^a (ppbC)	HC/NO$_x$ (ppbC/ppb)	Seed^b	Seed mass^c (µg m^{-3})	OM$_0$^{d} (µg m^{-3})					
12/5/2020 (E)	1800	12.8	NS	-	2	281-302	46-98	13.4	19.9	3(a), 4(a)
3/6/2019 (W)	1500	11.0	SA	30	2	290-315	28-91	9.6	31.9	3(d)
1/16/2021 (E)	1500	12.5	dAS	50	2	275-296	24-86	7.9	21.3	3(e)
1/16/2021 (W)	1500	12.5	wAS	50	2	276-296	60-93	20.07	21.3	3(e), 4(d)
1/19/2021 (E)	1500	12.2	wAS	120	3	274-300	47-88	22.8	20.4	3(f)
1/4/2021 (E)	1500	2	SA	30	4	277-300	26-88	8.9	21.1	3(b), 4(b)
1/4/2021 (W)	1500	2.3	NS	-	4	278-301	32-93	6.6	21.1	3(c), 4(c)
1/28/2021 (E)	1500	6.8	wAS	30	1.5	279-297	31-91	10.1	23.6	3(g)

The aging degree of hydrocarbon are reflected in the gas mechanism by using aging factor which is calculated from the concentration of RO$_2$ and HO$_2$ and initial injected hydrocarbon concentration and applies to the lumping species in the UNIPAR model (see section 3 in the manuscript). In addition, the TUVR data measured in spring (3/6/2021) and winter (12/5/2020) were added in Fig. S6 (Figure S5 in the revised manuscript) to show the difference in the sunlight intensities.

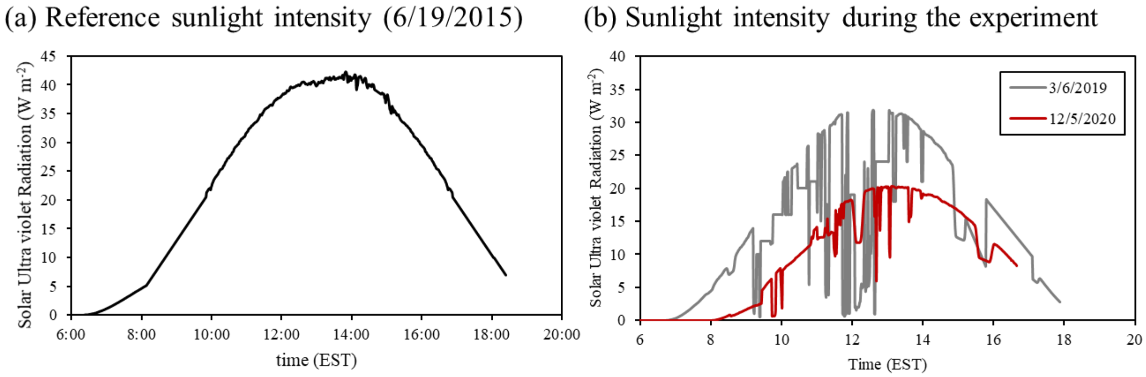

Figure S5. Time profile of sunlight total ultra-violet radiation (TUVR) measured in the UF-APHOR on (a) 6/19/2015 for the reference sunlight intensity, and that on (b) 3/6/2019 and 12/5/2020 during the experiments.

4. Line 55**:** As written, it is not clear what parameter(s) the negative biases from wall losses are affecting in SOA models.

   Response:
   The model parameters to form SOA are typically determined on the basis of a mass balance by using chamber data. Thus, the deposition of organic vapor to the chamber wall can cause a negative bias on SOA formation. The manuscript has been revised to respond to this comment.
   "The deposition of organic vapor onto the reactor wall can cause the negative bias in SOA prediction because SOA model parameters are typically determined on the basis of a mass balance by using chamber data. (Matsunaga and Ziemann, 2010;Zhang et al., 2014;Yeh and Ziemann, 2015;Krechmer et al., 2016;Huang et al., 2018)."

5. Line 158, "FS is 1 in SA and 0.33 in AS, indicating the aerosol acidity." It is not immediately clear what the authors mean by "indicating" in this context. Is it meant that fractional sulfate can be used as a proxy for initial aerosol acidity? What ranges of FS would be expected for ambient aerosol?

   Response:
   Yes, in this study, fractional sulfate was used as a variable which can indicate the aerosol acidity. In the UNIPAR model, the FS value along with humidity was applied to calculate the proton concentration in aerosol and excess acidity, which are linked to the acid-catalyzed reaction of organic species in the presence of salted aqueous solution. Based on the previous field study measured by Jang et al. (2020), FS ranges from 0.334 (neutral) to 0.8 in Florida.
   L161 is updated in the revised manuscript:
   "In the model, FS, introduced to determine aerosol acidity, ranges from 0.334 for AS to 1 for SA."

6. Line 83, "before sunrise:" given that vapor wall losses are a major feature of this paper, do the authors expect that the amount of time that the initial gasoline vapor spends in the chamber prior to photoreaction will contribute to variance in yields?

   Response:
   The GWP process of major aromatic hydrocarbons in gasoline is negligible due to high volatility of aromatic hydrocarbons. The oxidation of aromatic hydrocarbons begins with sunrise and thus, no semivolatile oxygenated product appears before sunrise.

7. Line 84: Similar to a broader comment above, does the experimental run in March have any notably different behavior compared to the runs that took place in January/December?

Response:

There was a difference in meteorological conditions, such as temperature, humidity, and sunlight intensity, between the experiments due to season and cloud coverage. In general, dual chamber experiments are performed under the same meteorological condition with two different experimental conditions such as HC/NO$_x$ ratios, seed conditions, or initial HCs. For gasoline experiments, the experiment was not repeated under the same experimental condition in different seasons. However, we performed sensitivity test of SOA formation to environmental variables (temperature and humidity) in Fig. 6 (Fig.7 in the revised manuscript).

8. Section 4.1: This section refers explicitly to multiple figures and tables in the supplemental information and is difficult to interpret without having these figures open; as such, it would likely make sense that some of this information is moved into the body of the manuscript itself. Further, the first paragraph has a majority of its text describing these figures, making it difficult to parse the main assertions and conclusions that the authors are trying to articulate. This section should be reworked to improve its readability.

Response:

Figure S5 has been moved to the manuscript as Fig. 3 and its description was also added in the revised manuscript (Section 4.1).

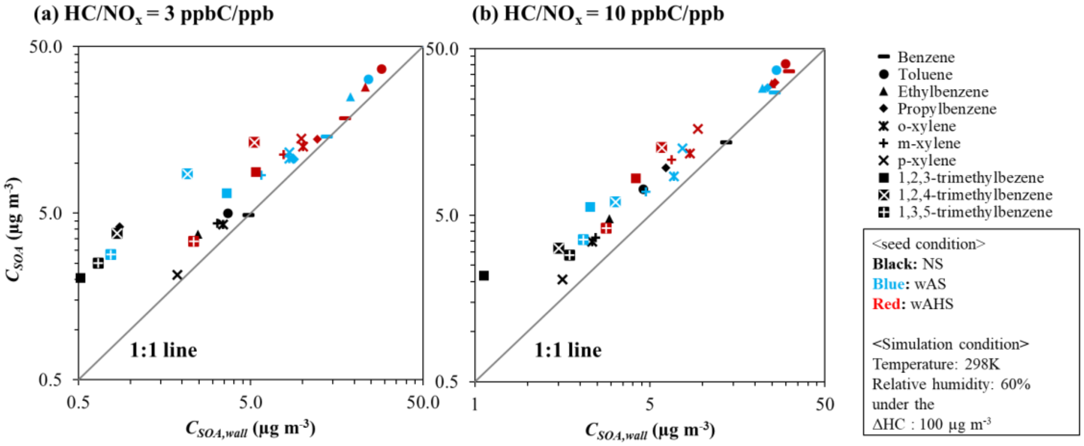

Figure 3. The simulated C_{SOA} and $C_{SOA,wall}$ for 10 different aromatic HCs at the given reference conditions. The SOA formation is simulated at the 298K and 60% at a given sunlight intensity (Fig. S5). The concentration of initial HC is determined to consume 100 µg m^{-3} of HC at 5PM. The initial HC ppbC/NO$_x$ ppb sets to 3 and 10 for high NO$_x$ level and low NO$_x$ level, respectively. SOA masses are also obtained at 5PM. The color of the symbol indicates the seed conditions: black, blue, and red for non-seeded (NS), wet ammonium sulfate (wAS), and wet ammonium hydrogen sulfate (wAHS), respectively.

9. Section 4.2: While it is true that the majority of the observed chamber data shows agreement with the authors' OM$_T$ model, it may be helpful to include percentage errors or residuals between model and data. Potential trends in model inaccuracy across different chamber experiments and/or times-of-day would be easier to infer.

Response:

The averaged deviations of simulation from experimental data have been added to Fig. 3 (Fig. 4 in the revised manuscript) caption and reads now,
"The averaged deviations of simulation from experimental data are (a) 2%, (b) -14%, (c) -32%, (d) -22% and -24%, (e) -10%, and (f) 10%."

10. Line 306: When the authors refer to "uncertainty," is it correct to state that they are performing a sensitivity analysis of sorts similar to what they perform in the preceding section, though by adjusting (phenomenological) model parameters rather than environmental conditions? Do the authors expect similar sensitivity trends if GWP factors are taken into account?

    Response:
    The uncertainty in this section is to discuss the sensitivity of SOA formation to model parameters such as vapor pressure (P_L°), activity coefficient (γ_{in}), reaction rate constant organic ($k_{o,i}$) or inorganic phase ($k_{AC,i}$). These uncertainties are tested with model parameters in the absence of GWP (GWP free). The tendency of these SOA mass uncertainties in Fig. 6 (Fig. 7 in the revised manuscript) is similar to that in the presence of GWP, previously reported in numerous studies (Zhou et al., 2019;Yu et al., 2021;Beardsley and Jang, 2016;Im et al., 2014) and reads now.
    "Figure 7 represents the uncertainties of the SOA prediction caused by the uncertainties in the major model parameters ($p_{L,i}^{\circ}$, $\gamma_{in,i}$, $k_{o,i}$, and $k_{AC,i}$) in the absence of GWP. The tendency of these SOA mass uncertainties in the presence of GWP (Zhou et al., 2019;Yu et al., 2021;Beardsley and Jang, 2016;Im et al., 2014) was similar to those in Fig. 6 (Fig. 7 in the revised manuscript)."

Technical Corrections:

1. Line 38: Missing space on "bias."

   Response:
   The manuscript has been revised based on this comment.
   L42 in the revised manuscript: "Much effort has been given to reduce the model–measurement discrepancies by adding missing SOA precursors (McDonald et al., 2018), including heterogeneous reactions (Carlton et al., 2010), and correcting the SOA model parameters by considering gas–wall partitioning (GWP) bias (Cappa et al., 2016; Baker et al., 2015; Hayes et al., 2015)."

2. Line 82: "flam ionization" should be "flame ionization."

   Response:
   The manuscript has been revised based on this comment.
   L87 in the revised manuscript: "Based on the gas chromatography-flame ionization detector (GC–FID, HP-5890/Agilent Technologies 7820A) analysis of injected gasoline vapor, 30% of carbons in the gasoline were from single-ring aromatic HCs (Fig. S1)."

3. Line 350: "…but oligomer is less favorable…" should be checked for grammar.

   Response:
   The manuscript has been revised based on this comment.
   L366 in the revised manuscript: "Increased polarity increases organic solubility in the salted aqueous phase. However, oligomer is relatively unfavorable to be mixed with salted aqueous phase, in

comparison to the low MW organics, because oligomers require a large combinational energy for mixing with small water molecules."

4. Line 351: "This is because…" should have been checked for grammar.

   Response:
   The manuscript has been revised based on this comment.
   L366 in the revised manuscript: "Increased polarity increases organic solubility in the salted aqueous phase. However, oligomer is relatively unfavorable to be mixed with salted aqueous phase, in comparison to the low MW organics, because oligomers require a large combinational energy for mixing with small water molecules."

5. Figure 2: There is no indication in text or in the caption of which set of markers corresponds to which dataset.

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

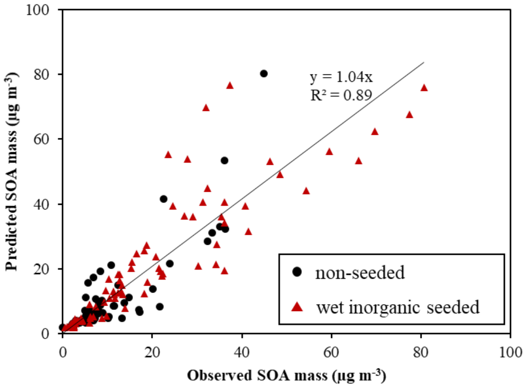

Figure 2. The linearity of predicted SOA mass (μg m^{-3}) using UNIPAR-CB6r3 and observed SOA mass (μg m^{-3}) in the absence and the presence of wet inorganic seed. SOA mass was produced via the photooxidation of various aromatic HCs (Table S2) in the UF-APHOR chamber.

6. **Figure 3**: What does the 9% error refer to? Instrumental resolution? Standard deviation/error across multiple samples? It would make more sense to present this error in absolute terms (i.e., in units of μg/m^{-3}).

   Response:
   As mentioned in the figure caption, the error (9%) was estimated with the instrumental uncertainty in the OC/EC analyzer. The error was estimated by considering particle wall loss and gas dilutions from the instrumental uncertainty.

References:

Cappa, C. D., Jathar, S. H., Kleeman, M. J., Docherty, K. S., Jimenez, J. L., Seinfeld, J. H., and Wexler, A. S.: Simulating secondary organic aerosol in a regional air quality model using the statistical oxidation model-Part 2: Assessing the influence of vapor wall losses, 16, 3041–3059, https://doi.org/10.5194/acp-16-3041-2016, 2016.

Beardsley, R., and Jang, M.: Simulating the SOA formation of isoprene from partitioning and aerosol phase reactions in the presence of inorganics, Atmospheric Chemistry and Physics, 16, 5993-6009, 10.5194/acp-16-5993-2016, 2016.

Im, Y., Jang, M., and Beardsley, R.: Simulation of aromatic SOA formation using the lumping model integrated with explicit gas-phase kinetic mechanisms and aerosol-phase reactions, Atmospheric Chemistry & Physics, 14, 2014.

Yu, Z., Jang, M., Zhang, T., Madhu, A., and Han, S.: Simulation of Monoterpene SOA Formation by Multiphase Reactions Using Explicit Mechanisms, ACS Earth and Space Chemistry, 2021.

Zhou, C., Jang, M., and Yu, Z.: Simulation of SOA formation from the photooxidation of monoalkylbenzenes in the presence of aqueous aerosols containing electrolytes under various NO x levels, Atmospheric Chemistry and Physics, 19, 5719-5735, 2019.