Manuscript: egusphere-2023-2461

Reviewer #3

General comment. The manuscript "Dual roles of inorganic aqueous phase on SOA growth from benzene and phenol" provides coupled experimental and modelling evidence of the suppression of atmospheric oxidation capacity and SOA growth due to the formation of persistant peroxy radicals formed during the production of benzene and phenol derived SOA. The Heterogeneous Persistant Phenoxy Radical Model was derived with a new explicit mechanism for the formation of HOM and H-PPR and utilised in the UNIPAR model to predict the formation of SOA from multiphase reactions of phenol and benzene. The addition of H-PPR into model was found to increase suppression of SOA growth with this suppression found to further increase with increasing aerosol acidity.

Response to the general comment: Thank you for your thoughtful comments on this manuscript. Due to your comment, the quality of this paper has been improved much.

Comment 1. While the importance of this work on urban areas specifically is mentioned, I don't feel this is quantitively explored enough in the implications section. I would suggest restructuring this section as the conclusion currently reads more like a discussion to me with new ideas still being introduced (i.e. ln 406" Phenol is the most abundant first-generation product from the oxidation of benzene…") and a lot of use of generalizations in language such as "about" or "generally". Slightly more quantitative implications would help to cement the importance of this work. What urban areas of the world is this most likely to effect? Areas with more biomass burning and wildfires or areas such as Chinese megacities and haze dominated regions?

> **Response:** The section for Conclusion and Atmospheric Implication has been reconstructed to provide better flow and quantitative interpretation, and the revised modified paragraphs reads now,
>
> "Fundamentally, biomass burning under open flame is performed at low temperature and produces very low NO (Simoneit, 2002; Mebust and Cohen, 2013; Xu et al., 2021). The chemistry slows to a standstill without NO_x and thus halts ozone formation although gaseous HCs are abundant. When these fire plumes mix into urban atmospheres abundant in NO_x, ozone formation becomes active, impacting the air quality of the city. Chamber data of this study mimics the phenol oxidation in the presence of NO_x. In addition, hygroscopic inorganic aerosols comprising of nitrate, sulfate and ammonium ions are available in the city environment rich in NO_x, SO_2 and NH_3. When wildfire plumes mix in city air, their phenolic compounds interact with NO_x and hygroscopic inorganic aerosol. The results from this study suggest that PPR produced during the atmospheric process of phenolic compounds in wildfire plumes can retard the atmospheric oxidation in urban environments. The SOA simulation with the low concentrations of phenol and typical atmospheric tracer gas (formaldehyde, acetaldehyde) in Fig. 5 shows that phenol SOA is considerably suppressed even with a small amount of wet inorganic aerosol

raging from weakly to neutral acidity. For example, phenol SOA mass decreases by 12% with 5 ppb of ammonium hydrogen sulfate (FS=0.5) (Fig. 5(A)) and the SOA mass from the mixture of phenol and benzene decreased by 28% (Fig. 5(C)).

The impact of NO_x on SOA formation appeared to be negative as shown in Fig. 6 under high NO_x levels. A significant fraction of phenolic SOA is through HOM products and oligomeric matter. The contribution of HOM and oligomeric matter on SOA formation is generally higher with lower NO_x levels. Thus, phenol SOA and benzene SOA are relatively insensitive to temperature (Fig. 6) due to the high fraction of SOA mass being non-volatile. This result suggests that SOA from biomass burning is not substantially affected by temperature under low NO_x regimes. When the concentrations of NO_x drop in the high NO_x zone, SOA formation increases. The role of PPR on atmospheric oxidation capacity in the blending of wildfire smoke and urban pollutants needs to be studied under different NO_x levels.

A variety of phenolic compounds including phenol, cresol, catechol, methoxyphenols, dimethylphenols (Akherati et al., 2020; Bruns et al., 2016) can consist of more than 80% of the precursor HCs in wildfire smoke. These multifunctional phenolic compounds can also yield PPR as active scavengers for ozone (Section 3.2.2). To date, the impact of phenolic compounds on retardation of atmospheric aging of HCs in the city air has not been sufficiently studied. It is important to comprehend the formation mechanisms of PPR-like chemical species and their role on atmospheric oxidation capability to accurately predict the elevation of ozone and SOA and their peak time."

Comment 2. Section 4.1 – suggest slight restructuring/rewording for increased clarity as it is a bit difficult to follow at present.

> **Response:** The Section 4.1 was reconstructed based on the comment, see in manuscripts Ln. 270 to Ln.286, reads now:
>
> "Fig. 3 (A-L) shows gas simulations (phenol, benzene, ozone, NO, and NO_2) based on data collected in the UF-APHOR chamber. In the presence of wet-inorganic seed (i.e., wet-AS, AHS, and SA), both simulations and chamber data demonstrate a notable suppression in gas oxidation, specifically in ozone formation and the decay of phenol or benzene, compared to gas oxidation in non-seeded conditions. Fig. 3(B) and (H) show gas simulations for phenol and benzene oxidation in the presence of SA seed without the H-PPR mechanism, revealing a significant discrepancy between simulations and observations. Fig. 3(C) and (I) demonstrate enhanced gas simulations using H-PPR under identical experimental settings, highlighting the significance of H-PPR in precisely forecasting the oxidation of phenol or benzene in the presence of wet inorganic aerosol, as outlined in reactions R3-R5. Aside from phenol, catechols and nitrophenols, which are significant byproducts of phenol oxidation, can also participate in the PPR formation. Suppressed ozone levels can decrease the generation of OH radicals and slow down the aging of organic substances. Explicit gas simulations incorporating HOM and H-PPR show good agreement with observations.

Fig. 4(A-P) shows chamber-generated SOA mass from the photooxidation of phenol (Fig. 4(A-H)) or benzene (Fig.4(I-P)) under various inorganic seed conditions (Table 1), along with simulations of SOA formation using the UNIPAR model. Overall, an enhanced SOA simulation of phenol or benzene was conducted using precise gas simulation combined with HOM and H-PPR. Fig. 4(A) and (B) display non-seed phenol SOA, while Fig. 4(I) and (J) show non-seed benzene. Fig. 4 (C-H) displays SOA masses generated with inorganic seed (SA, AHS, wet- or dry-AS) for phenol, while Fig. 4 (K-P) shows the masses for benzene.

Fig. 4(C) and (G) show the significance of H-PPR mechanisms in predicting SOA for phenol, while Fig. 4(K) and (O) demonstrate this for benzene by comparing simulations with and without H-PPR. The suppression of SOA formation was greater with highly acidic aerosol.

The formation rate of PPR can be affected by the chemical composition of the aerosol medium. Mitroka et al. (Mitroka et al., 2010) reported that reactivity of the OH radical is considerably higher in polar, protic solvent than that in dipolar, aprotic solvent. Protic solvent is a hydrogen bond donor that stabilizes the transition state of the OH radical addition reaction. Thus, the reaction of phenols with the OH radical is more favorable in in phase than or phase. The radical scavenging ability of phenols by forming phenoxy radicals is in the order of pyrogallol > 1,2,4-benzenetriol >catechol > hydroquinone > resorcinol ≈ phloroglucinol (Thavasi et al., 2009). As shown in reaction R8, phenol in salted aqueous media reacts with OH(in) in a similar way with the OH addition to the aromatic ring in the gas phase to form intermediate product phenol_OH_int (in) (Fig. 2). Fig. S3 is the proposed mechanism to form phenoxy radical via the acid-catalyzed reaction. In addition, some organic products such as quinones can promote increased oxidants in aqueous acidic media. Quinones are well recognized for their ability to promote superoxide formation (Guin et al., 2011). Lowering pH increases the redox potential (Walczak et al., 1997) of quinone-hydroquinone. However, the reduction potential of oxygen can be lower in acidic condition and is advantageous for $O_2\bullet$-/$HO_2\bullet$ formation (Wei et al., 2022) (Section S4).

The importance of HOM on phenol SOA has been demonstrated in the previous study by Choi and Jang (Choi and Jang, 2022). For example, a large fraction of OMP in Fig. 4(A) is contributed by HOM. The contribution of HOM to SOA mass increases with decreasing NO levels. The systematic evaluation of the UNIPAR model integrated with the explicit gas mechanisms will be performed via the model sensitivity to various environmental variables (i.e., NO_x levels, seed, temperature, and humidity) in Section 4.2."

Comment 3. Adding in the factors of suppression for the different model scenarios may help to add context to level of suppression of SOA growth exhibited. At present, throughout the manuscript this is not directly given a number.

> **Response:** We added the suppression SOA formation with and without H-PPR in Fig. 5. Please find the response to comment 1.

Comment 4. Have you considered natural emissions of benzene and phenol such as over polar oceans or in the marine boundary layer? (Wohl et al., 2023 Sci. Adv.)

Response: Thank you for pointing out the flux of benzene from oceans or in the marine boundary layer. We cited the recommended paper in introduction.

Comment 5. How competitive is NO_3 oxidation of phenol to give C_6H_5O compared to the reactions with OH and O_3? Is this significantly fast as a dark reaction to be considered important? When NO_3 is the oxidiser is the oxidation capacity of the system still suppressed with increasing aerosol acidity?

Response: Thanks for the comment on NO_3 radical. In order to response to the reviewer's comment, we perform the integrated reaction rate (IRR) analysis. The IRR analyses demonstrate that (1) H-PPR production is important to form PPR in the presence of wet seed (description in Section 4.2.1) and (2) the nitrate radical oxidation with phenol is important to form PPR during nighttime (description in Section 4.2.2). This reads now,

Section 4.2.1 (2nd paragraph)

"The DISMACC box model flatform of this study is equipped with the integrated reaction rate (IRR) analysis technique, which can show the chemical reaction flow in the oxidation mechanisms. Based on the IRR analysis, the production of PPR is mainly contributed by the reaction of phenol with OH radicals in gas phase and the catechol H-PPR mechanism. The phenoxy radical production via the phenol H-PPR path is trivial due to the low partitioning of phenol into the aqueous phase. Unlike phenol, catechol, a major product of phenol oxidation, can yield the semiquinone radical (PPR of catechol) via the heterogeneous reaction mechanism. For example, in the presence of SA seed (Fig. 5(A)), the contribution of the catechol H-PPR path is 1.22 times greater than that of the gas-phase reaction of phenol with OH radicals. In the presence of wet-AS seed, the contribution of the catechol H-PPR path is 20% of that from the gas-phase reaction of phenol with OH radicals."

 Section 4.2.2 (4th paragraph)

"Of the total PPR production, the contribution of daytime phenol oxidation with nitrate radicals is only 0.1% of that from the phenol oxidation with OH radicals in the high NO_x condition (VOC ppbC/NO_x ppb = 2) of Fig. 6(B). However, the contribution of nitrate radical mechanism to form PPR increases in the absence of sunlight. For example, the contribution of nitrate radicals on PPR is nearly 30% of that with OH radicals at a given simulation condition under the high NO_x condition between 4PM to 5PM (Fig. 6(A)). This simulation result suggests that the nitrate radical oxidation with phenol is important to form PPR during nighttime."

Minor corrections:

Comment 1. Throughout the manuscript the consistency of inclusion of units and unit formatting needs to be checked.

> **Response:** Units and formatting have been corrected thoroughly.

Comment 2. Throughout the manuscript there is repeated mentions of other phenolic compounds. In ln 281 it is mentioned that "The radical scavenging ability of phenols by forming phenoxy radicals is in the order of pyrogallol > 1,2,4- benzenetriol >catechol > hydroquinone > resorcinol ≈ phloroglucinol". This being said, why was the focus of the study not expanded to include some of the more active phenols, especially as phenol can form.

> **Response:** Phenol is a starting precursor of this study. Phenol oxidation yields the multi-hydroxy substitute phenols, and their product can produce PPR via H-PPR mechanisms. For example, the catechol H-PPR mechanism is included in the gas mechanism in addition to phenol. The gas mechanism also produces pyrogallol, but this concentration is trivial.

Comment 3. Consistency in nomenclature is needed. For example pyrogallol and catechol are not given in chemical nomenclature, but 1,2,4-benzenetriol is. Suggest changing to hydroxyhydroquinone or changing the others, ie pyrogallol to 1,2,3-benzenetriol, or catechol to 1,2- benzenediol.

> **Response:** The nomenclature of multi hydroxy benzenes has been corrected using the IUPAC guideline except catechol (1,2-dihydroxybenzene).

Comment 4. I suggest adopting a consistent colour for benzene and for phenol in all figures. Being different colours in every figure reduces readability.

> **Response:** Colors in Figs.3, 4, and 8 have been changed.

Technical revisions:

Abstract:

Comment 1: Missing author affiliation numbers. Add in what the implication of this research is atmospherically.

> **Response:** This has been added.

Comment 2: Is the mention of NO_x limited regimes worth highlighting more?

> **Response:** The NO_x regime originates from the relative importance of the reaction between NO_2 and OH compared to the reaction between hydrocarbons and OH radical. In general, the reaction of NO_2 with OH radical is more important than the reaction of hydrocarbon with OH in the region of the VOC ppbC/NO_x ppb ratio less than 5. In the

high NO$_x$, OH radical is consumed by NO$_2$ and the products include more organonitrate and PANs, which can produce SOA by the gas-particle partitioning process. In addition, HOM production is high in the low NO$_x$ region.

Comment 3: Add in what the implication of this research is atmospherically.

Response: This has been added.

Introduction:

Comment1 : Add in some statistics and refs of the prevalence of benzene and phenol atmospherically.

Response: The emission of phenol from biogenic burning is included with the reference, and reads now,

"In addition, a significant fraction (20%) of oxygenated aromatic, emitted from biomass burning, is phenol (Akherati et al, 2020)."

Comment 2: Ln 35 – where globally is represented by 20 % and where 90 %?

Response: Citation has been added and reads now in the refence of the revised manuscript,

"Kanakidou, M., Seinfeld, J. H., Pandis, S. N., Barnes, I., Dentener, F. J., Facchini, M. C., Van Dingenen, R., Ervens, B., Nenes, A., Nielsen, C. J., Swietlicki, E., Putaud, J. P., Balkanski, Y., Fuzzi, S., Horth, J., Moortgat, G. K., Winterhalter, R., Myhre, C. E. L., Tsigaridis, K., Vignati, E., Stephanou, E. G., and Wilson, J.: Organic aerosol and global climate modelling: a review, Atmos. Chem. Phys., 5, 1053–1123, https://doi.org/10.5194/acp-5-1053-2005, 2005."

Comment 3: Ln 45 – references needed

Response: Citation has been added into the revised manuscript.

"Borrás,E., Tortajada-Genaro, L. A.: Secondary organic aerosol formation from the photo-oxidation of benzene, Atmos. Environ., 47, 154-163, https://doi.org/10.1016/j.atmosenv.2011.11.020, 2012."

Comment 4: Where is the benzene oxidation path important? Why is it hard to study benzene oxidation specifically?

Response: The benzene oxidation rate is relatively very slow (1.22×10-12 cm3 molecules-1 sec-1 at 298 K). Therefore, the consumption of the benzene is little and SOA formation is low.

Comment 5: Expand the mention of wildfire SOA to mention briefly atmospheric implications.

    Response: In the 3rd and 5th paragraphs in Section "5. Conclusion and Atmospheric Implications", wildfire SOA has been discussed.

Comment 6: Ln 66- what relative humidity are you defining as "wet" and is it consistent over all experiments?

    Response: The definition of wet is determined based on the inorganic phase state. The wet inorganic aerosol contains water, but dry aerosol is efflorescent with no water. The UNIPAR model calculates efflorescence relative humidity (ERH) and water content and applies aerosol chemistry in the aqueous phase. Please find model description Section 3.1.

Comment 7: Ln 69 – add more recent references for aerosol acidity experiments

    Response: More references have been added in the revised manuscript, reads now,

    "Deng, Y., Inomata, S., Sato, K., Ramasamy, S., Morino, Y., Enami, S., and Tanimoto, H.: Temperature and acidity dependence of secondary organic aerosol formation from α-pinene ozonolysis with a compact chamber system, Atmos. Chem. Phys., 21, 5983–6003, https://doi.org/10.5194/acp-21-5983-2021, 2021."

    "Surratt, J. D., Lewandowski, M., Offenberg, J. H., Jaoui, M., Kleindienst, T. E., Edney, E. O., and Seinfeld J. H.: Effect of Acidity on Secondary Organic Aerosol Formation from Isoprene. Environ. Sci. Technol., 41, 5363-5369, DOI: 10.1021/es0704176, 2007."

Model description:

Comment 1: Ln 131 – typo, correct to UNIPAR

    Response: This has been corrected.

Comment 2: Figure 2 is too cramped with the ending 'e' of 'intermediate' cut off

    Response: This has been corrected.

Results and Discussion (Section 4.1):

Comment 1: Figure 3 – none of the axes are labelled or given units, these also need to be added to the figure caption.

Response: The unit of the axes is labeled in fig 3 (A) only. For better readability, the figure caption has been changed and reads now,

"The time profiles of observations and the prediction for concentrations of NO, NO$_2$, and O$_3$ and hydrocarbons (Table 1). The x-axis represents time (EST), the first y-axis represents the concentration (ppb) of gas species, and the second y-axis represents the hydrocarbon concentration in gas phase (ppb) as shown in (A). "HC" and "HC_exp" demote the gas simulation of hydrocarbons used in experiment and measurement of hydrocarbon used in experiment, respectively. The error associated with NO, NO$_2$, and O$_3$ are 2% and not visible in this Figure."

Comment 2: Both Figure 3 and 4 need to be reworked to help readability. I suggest splitting the figure into benzene and phenol, or perhaps phenol have dashed lines and benzene filled. At present the figure is hard to digest. The figure titles are also overpowering and the legend is too small and needs reordering so the predictions and corresponding experiments are side by side.

Response: We decided not to split the figures 3 and 4 into benzene and phenol. By this way, reader can compare benzene and phenol.

Comment 3: Ln 264 –How is improved quantified? What is this in relation to?

Response: The model simulation is evaluated by comparing predictions with chamber data. In order to clarify this, the sentence has been rewritten, and reads now in the 2nd paragraph of Section 4.1,

"Under the same experimental conditions, simulations with H-PPR in Fig. 3(C) and (I) well predict chamber data showing the importance of H-PPR (reactions R3-R5)."

Comment 4: Ln267 – should this be explained explicitly earlier as an indirect amplification of the scavenging of O$_3$?

Response: Section 4.1 has been reorganized to provide better flow. Please find the response to comment 2 (major comment).

Comment 5: Ln 272 – "accurate gas simulation" – why is it defined as accurate?

Response: Word "accurate" has been changed to "improved".

Comment 6: Ln 277 – how are you defining "highly acidic aerosol"?

Response: Word "highly" has been removed.

Comment 7: Ln 278 to 283 - feel a bit out of place.

Response: This has been done.

Comment 8: Ln 286 -289 – unclear why this is said here.

> **Response**: This explains the multi-functional phenols from phenol oxidation can promote the oxidants in aqueous phase, which could advantage the H-PPR mechanism.

Comment 9: Figure 7 – axis C label and legend font colour should be black not grey. And plot A is a side-by-side boxplot while B and C are not.

> **Response**: This has been done.

Results and Discussion (Section 4.2):

Comment 1: Ln 297 – Is "FS value" defined previously? If not, define here.

> **Response**: This has been defined before in Section 3.2.2.

Comment2 : Ln 299 – insert reference for deliquescence point of seed aerosol

> **Response:** The reference has been added in the revised manuscript, reads now,
>
> Peng, C., Chen, L., Tang, M.: A database for deliquescence and efflorescence relative humidities of compounds with atmospheric relevance, Fundamental Research, 2, 578-587, https://doi.org/10.1016/j.fmre.2021.11.021, 2022."

Comment 3: Ln 308 – why do you think that a larger conc of inorganic seed suppresses SOA mass? – for a given RH there is less water per seed particle? i.e. each surface has a thinner liquid microlayer?

> **Response:** The concentration of organic species in inorganic phase ($C_{in,i,}$) increase with the mass concentration of inorganic mass (M_{in}). M_{in} increase with more inorganic aerosol mass and high humidity as seen in equation below.
>
> $$C_{in,i} = \frac{K_{in}M_{in}}{1+K_{or,i}OM_T+K_{in,i}M_{in}} C_{T,i} \text{ (Eq.S9)}$$
>
> This equation has been added into the Section "S2 UNIPAR Model Structure" of SI.

Comment 4: Ln 325 – why was 30 ppb chosen for the initial concentration?

> **Response:** This was set to mimic real world environment.

Comment 5: Ln 336 – 2.82E-11 reformat as 2.82 10-11 and provide reference

> **Response:** Citation has been added and reads now in reference,

"Yee, L. D., Kautzman, K. E., Loza, C. L., Schilling, K. A., Coggon, M. M., Chhabra, P. S., Chan, M. N., Chan, A. W. H., Hersey, S. P., Crounse, J. D., Wennberg, P. O., Flagan, R. C., and Seinfeld, J. H.: Secondary organic aerosol formation from biomass burning intermediates: phenol and methoxyphenols, Atmos. Chem. Phys., 13, 8019-8043, 10.5194/acp-13-8019-2013, 2013."

Comment 6: Ln 227 – 1.2E-12 reformat as 2 10-12 and provide reference

Response: Citation has been added and reads now in reference,

"Kwok, E. S.C., Atkinson, R.: Estimation of hydroxyl radical reaction rate constants for gas-phase organic compounds using a structure-reactivity relationship: An update, Atmos. Environ. 29, Issue 14, 1685-1695, https://doi.org/10.1016/1352-2310(95)00069-B, 1995."

Comment 7: Ln 336 to 340 – Is this repeated information, is it needed here?

Comment 8 :Ln 350, Section 4.2.3 – is this section not also testing the senstivitiy, as opposed to the uncertainty?

Response: To clarify, section number has been changed. In the revised manuscript, sensitivity test in under Section 4.2 and uncertainty test is under Section 4.3.

Comment 9: Ln 355 – only the sensitivity of the benzene simulations are included here. What not also Phenol?

Response: Thank you for pointing out this. The missing description has been added to the revised manuscript, and reads now in Section "4.3 Uncertainty of SOA Formation to Model Parameters",

"Under the same condition, the change in the phenol SOA mass due to VP uncertainties ranges from -13% to 14%."