

## **Response to Reviewers' Comments**

**Dear Editor and Reviewers,**

Thank you very much for your efforts in handling and evaluating our submission.

The review comments are very helpful for improving the original manuscript. We have carefully considered and tried to address all of these comments in the revised manuscript. Below are the detailed point-by-point responses to the review comments. For clarity, the reviewer's comments are listed below in *black italics*, while our responses and changes in the manuscript are highlighted in **blue** and **red**, respectively.

We look forward to receiving a further evaluation of our work.

Best regards,

Guy Brasseur and co-authors

*The article titled "Characterizing Atmospheric Oxidation Capacity in China: Insights from Numerical Simulations" aims to provide a detailed analysis of the atmospheric oxidation capacity (AOC) in China, considering the changes in anthropogenic emissions over the past decade. The authors use the WRF-Chem model to simulate different parameters that influence AOC and investigate the impact of aerosols on surface ozone levels. The study also examines the contribution of various reactive species to AOC in different regions of China. The article provides a comprehensive analysis of AOC in China, considering various factors such as aerosol effects, photodissociation rates, and heterogeneous reactions. The objectives of the study are clearly stated, and the article follows a logical structure, making it easy to understand the research approach and findings. Given the increasing concern about air pollution in China, understanding AOC and its contributing factors is highly relevant. The article addresses an important topic and sheds light on the impact of aerosols and anthropogenic precursors on atmospheric chemistry which is in the scope of ACP. I recommend the paper published in ACP after minor revision. Here is a few suggestions that might help to improve the paper.*

**Response:** We thank the reviewer for the positive comments and constructive suggestions. We have addressed all of these comments and revised the original manuscript accordingly. Below are the itemized responses to the specific comments.

*Discussion:*

*(1) The study heavily relies on numerical simulations performed with the WRF-Chem model. While this approach provides valuable insights, the authors should have discussed the limitations of the model and the uncertainties associated with the simulations more meticulously by adding a paragraph instead of shortly discussing in 3.3.*

**Response:** We added some discussion about model limitations in resolutions in simulating the radical and ozone chemistry. The uncertainties discussed are associated with the model performance in the concentration of NO<sub>2</sub>, PM<sub>2.5</sub>, and specific VOCs and the potential effect on ozone calculation. The new text for the model validation is as follows. It is complemented by text in the supplementary information

### **3.3. Model validation**

In Figure S1, we compare the spatial distribution of the calculated surface concentrations of the Maximum Daily 8-hour average (MDA8) O<sub>3</sub>, as well as the monthly averages NO<sub>2</sub>, CO, and PM<sub>2.5</sub> (*Het-all* case) with available observational data from MEE for January and July 2018. In most cases, this comparison shows a good performance of the model with, however,

some discrepancies: an overestimation of summertime O<sub>3</sub> in central and western China associated with an underestimation of NO<sub>2</sub> in these regions, an underestimation of summertime O<sub>3</sub> in eastern China with a slight overestimation of NO<sub>2</sub> (Fig. S1). In the case of CO and PM<sub>2.5</sub>, the calculated concentrations are higher than the measured values in central China in both seasons.

One should stress here that a comparison of coarse resolution model output with local measurements made at ground stations is not straightforward and can only provide crude information. In order to alleviate the problem, we have combined the concentration values measured by different stations within a given area with the 36 km resolution model results. The areas including the individual stations in metropolitan areas are provided in Table 2.

The diurnal variation of NO<sub>2</sub>, O<sub>3</sub>, CO, and PM<sub>2.5</sub> in January and July for the four metropolitan areas selected in our study are compared with measurements from monitoring stations in Fig. S2 and S3. The model successfully simulates the diurnal variations of these chemicals. However, the summertime NO<sub>2</sub> concentration is overestimated in these urban areas. Summertime ozone concentrations are underestimated at night and overestimated during daytime. These discrepancies can be explained by the relatively lower NO<sub>2</sub> uptake coefficients used in our studies (Liu et al., 2019; Fu et al., 2019) and the coarse resolution of the model (Tie et al., 2010). An overestimation of the NO<sub>2</sub> concentration tends to broaden the area in which ozone is VOC-controlled.

The simulated CO concentration is slightly overestimated, which can be attributed to uncertainties in chemical boundary conditions and in the emissions (Liu and Wang et al., 2020). An overestimation of PM<sub>2.5</sub> is found in summer, which can be partially due to uncertainties in emissions and the mechanisms of secondary aerosol formation (Li et al., 2022). Model estimates of the NO, HONO, HCHO, OH, HO<sub>2</sub>, NO<sub>3</sub>, isoprene, ethane, and ethene mixing ratios for the base case are found in Fig. S4-S6. Calculated diurnal variations of surface NO, HONO, OH, HO<sub>2</sub>, and NO<sub>3</sub> are provided in Fig. S7-S11. Generally, based on the comparison of our simulated results with observed data in the literature, our simulated concentrations of OH, HO<sub>2</sub>, HONO, and HCHO match relatively well with the observational data. The calculated aerosol surface area density is shown in Fig. S12. The values calculated in eastern China are considerably higher during wintertime ( $2.5$  to  $3 \times 10^{-5}$  cm<sup>2</sup> cm<sup>-3</sup>) than during the summer ( $0.7$  to  $1.0 \times 10^{-5}$  cm<sup>2</sup> cm<sup>-3</sup>).

The validation of the model regarding volatile organic compounds is not easy to perform because of the short lifetime of most of these species, the inhomogeneity in their emissions, the complexity of the chemical processes involved, and the lack of observational data. In China, only a few stations report continuous measurements of VOCs. The comparison is made particularly difficult with a model whose grid size is equal to 36 km. Therefore, as an

illustrative example, we show in Fig. S13 of the Supplementary material, a comparison of the calculated and observed diurnal variation in the mixing ratio of ethane, propene, isoprene, ethane, propane, benzene, toluene, and xylene at the Hok Tsui site (Hong Kong) in January 2018. The discrepancies in the calculated concentrations of anthropogenic VOCs and of biogenic isoprene lead to inaccuracies in the calculated concentrations of secondary organic species such as formaldehyde as well as in the calculation of the OH reactivity ( $VOC^R$ ) and of the atmospheric oxidation capacity ( $AOC$ ).

More detailed information on the model validation is provided in the Supplementary Information.

(2) *Table 1: Please provide the exact rate constants of each reaction.*

**Response:** We have added the reaction rate constants for each reaction in Table 1 of the paper with appropriate references.

(3) *Line 272: Distinct species have different gas-phase diffusion coefficients. 0.247 only applied to HO<sub>2</sub>. Please explain how the simulation's gas-phase diffusion coefficients worked.*

**Response:** In this study, we chose 0.247 to be the gas-phase diffusion coefficient for HO<sub>2</sub> aerosol uptake (Xue et al., 2016). For other gas-phase diffusion coefficients, we selected the value of 0.1, which is consistent with the modeling studies (Gaubert et al., 2020; Liu and Wang., 2020). We clarify our statement as:

$D[\text{cm}^2 \text{ s}^{-1}]$  is the gas-phase diffusion coefficient, with the value of 0.247 for HO<sub>2</sub> uptake (Mozurkewich et al., 1987; Xue et al., 2016) and 0.1 for NO<sub>2</sub>, NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> uptake (Gaubert et al., 2020; Liu and Wang., 2020).

Xue, L., Gu, R., Wang, T., Wang, X., Saunders, S., Blake, D., Louie, P. K. K., Luk, C. W. Y., Simpson, I., Xu, Z., Wang, Z., Gao, Y., Lee, S., Mellouki, A., and Wang, W.: Oxidative capacity and radical chemistry in the polluted atmosphere of Hong Kong and Pearl River Delta region: analysis of a severe photochemical smog episode, *Atmos. Chem. Phys.*, 16, 9891–9903, <https://doi.org/10.5194/acp-16-9891-2016>, 2016.

Gaubert, B., L. K. Emmons, K. Raeder., Correcting model biases of CO in East Asia: impact on oxidant distributions during KORUS-AQ, *Atmos. Chem. Phys.*, 20, 14617-14647, <https://doi.org/105194/acp-20-14617-2020>, 2020.

Liu, Y. and Wang Tao, Worsening urban ozone pollution in China from 2013 to 2017 – Part 2: The effects of emission changes and implications for multi-pollutant control, *Atmos. Chem.*

(4) Line 280: *The case of a large abundance of TMI in the aerosol liquid phase, which would result in the outcome of HO<sub>2</sub> absorption being predominantly H<sub>2</sub>O, was put forth by Song et al. in 2021. The HO<sub>2</sub> uptake products are not ambiguous. Please refer to Mao et.al, 2013 and Mao et.al, 2017 for more information on the HO<sub>2</sub> uptake product as Mao et.al, 2013 has studied the potential reaction routes in detail. A test on how HO<sub>2</sub> uptake produces H<sub>2</sub>O<sub>2</sub> should be added.*

**Response:** To test the different impacts of HO<sub>2</sub> uptake on H<sub>2</sub>O and H<sub>2</sub>O<sub>2</sub>, two additional model cases with the HO<sub>2</sub> uptake producing H<sub>2</sub>O<sub>2</sub> were performed for conditions corresponding to January and July 2018. The differences in the calculated surface mixing ratio of OH, HO<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, and ozone for the two different assumptions are shown in Figure S21. When the HO<sub>2</sub> uptake produces H<sub>2</sub>O<sub>2</sub>, an increase in H<sub>2</sub>O<sub>2</sub> concentration is produced by the model in both January (Figure S21e) and July (Figure S21f) of 2018. Consistently, the simulated concentration of HO<sub>2</sub> is enhanced (Figure S21 c, d), resulting from the photolysis of H<sub>2</sub>O<sub>2</sub>. However, there are no clear and consistent changes in the concentration of the OH radical (Figure S21 a, b) and of ozone (Figure S21 g, h). We added the following text:

Finally, we assess how the assumption made on the product of the HO<sub>2</sub> uptake influences our model results. Figure S21 in the Supplementary Information shows the differences in calculated near-ground mixing ratios of OH, HO<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, and ozone when the heterogenous conversion of HO<sub>2</sub> is assumed to produce hydrogen peroxide rather than water molecules.

Two references (Mao et al., 2013; Mao et al., 2017) and the difference between the two different assumptions were added to the manuscript and the supplementary information (In Figure S21).

Mao, J., Fan, S., Jacob, D. J., Travis, K. R. Radical loss in the atmosphere from Cu-Fe redox coupling in aerosols. *Atmospheric Chemistry and Physics*, 13(2), 509-519. <https://doi.org/10.5194/acp-13-509-2013>, 2013.

Mao, J., Fan, S., Travis, K. R., Horowitz, L. W. Soluble Fe in aerosols sustained by gaseous HO<sub>2</sub> uptake. *Environmental Science & Technology Letters*, 4(3), 98-104. <https://doi.org/10.1021/acs.estlett.7b00017>, 2017.

(5) *Technical comments. Line 49 : What does "presence of aerosols" mean? The atmosphere always contains aerosols. Please provide the range of aerosol concentrations that would either increase or decrease ozone concentration.*

**Response:** We modified the sentence as follows:

The model shows that the aerosol effects related to extinction and heterogeneous processes produce a decrease in surface ozone of approximately 8-10 ppbv in NO<sub>x</sub>-limited rural areas and an increase of 5-10 ppbv in VOC-limited urban areas. In this later case, the ozone increase is noticeable for aerosol concentrations ranging from 20 to 45 μg/m<sup>3</sup> in July 2018 (Figure S3 b).

*(6)Line 431: At night, the oxidizing capacity is due to the oxidation by NO<sub>3</sub> and O<sub>3</sub>. Please add references.*

**Response:** Two references were added:

Brown, S. S., and Stutz, J. Nighttime radical observations and chemistry. *Chemical Society Reviews*, 41(19), 6405– 6447. <https://doi.org/10.1039/C2CS35181A>, 2012.

Ng, N. L., Brown, S. S., Archibald, A. T., Atlas, E., Cohen, R. C., Crowley, J. N. Nitrate radicals and biogenic volatile organic compounds: Oxidation, mechanisms, and organic aerosol. *Atmospheric Chemistry and Physics*, 17(3), 2103– 2162. <https://doi.org/10.5194/acp-17-2103-2017>, 2017.

*(7)Line 830: Due to its low latitude, Shenzhen experiences a meteorological summer season (monthly average temperatures above 22 °C) from April to October. The compensation mechanism was crucial, despite the fact that this particular citation could not support this claim.*

**Response:** We have added a sentence stating that such a compensating mechanism was highlighted by Qu et al. (2023). The sentence is

“Such a compensation mechanism was highlighted by Qu et al. (2023) based on their model study performed in the YRD region for different seasons”.

Qu, Y., Wang, T., Yuan, C., Wu, H., Gao, L., Huang, C., Xie, M. The underlying mechanisms of PM<sub>2.5</sub> and O<sub>3</sub> synergistic pollution in East China: Photochemical and heterogeneous interactions. *Science of The Total Environment*, 873, 162434. <https://doi.org/10.1016/j.scitotenv.2023.162434>, 2023.

*(8)Line 1054-1061:The article's primary indicator of interest was AOC. In other works, the author compared AOC data. Please be detailed in your analysis and explain how the data differs or is comparable to that in the article.*

**Response:** The calculation of *AOC* based on our simulated results is consistent with the definition adopted in the compared studies (Feng et al., 2021; Liu et al., 2022; Zhu et al., 2020;). Our calculated *AOC* is therefore comparable with the observed studies.