Detailed Response to Reviewers' comments
Manuscript Number: egusphere-2025-4355
Manuscript Title: An Observation-Based Methodology and Application for Future Atmosphere Secondary Pollution Control via an Atmospheric Oxidation Capacity Path Tracing Approach
Note: The Changes of reviewer's suggestion in the revision manuscript were indicated by the red font.

Reviewer #2: The manuscript of "An Observation-Based Methodology and Application for Future Atmosphere Secondary Pollution Control via an Atmospheric Oxidation Capacity Path Tracing Approach" presents a novel "Atmospheric Oxidation Capacity Path Tracing" (AOCPT) approach to address the persistent challenge of synergetic O_3 and $PM_{2.5}$ control in industrial regions. The methodology is scientifically sound, and the manuscript is generally well-written. But before publication, some details need to be explained. Overall, it is recommended to make minor modifications.

Response:

We thank the reviewer for the positive comments. For the comments from reviewers, we have revised the manuscript as better as we can. Please find our point-to-point responses below.

1. Can this AOCPT approach be directly applied to other seasons (e.g., winter, when AOC is lower) or non-industrial urban areas?

Response:

We appreciate this insightful question regarding the generalizability of our method. The AOCPT approach is designed as a universal framework based on fundamental physicochemical mechanisms, making it applicable to diverse seasons and urban typologies. The reasons are as follows:

(1) The chemical mechanism of AOCPT approach has universality. The core of the AOCPT approach (the OBM module) relies on the Master Chemical Mechanism (MCM 3.3.1), which explicitly describes the reaction kinetics of thousands of species (Jenkin et al., 2015; Wolfe et al., 2016). Since kinetic rate constants (k) are functions of temperature and pressure, the model inherently accounts for seasonal variations (e.g., lower reaction rates in winter) without requiring structural changes. Previous studies have successfully applied MCM-based box models to investigate pollution formation mechanisms across different seasons R(Yan et al., 2025; Yang et al., 2024).

(2) The source apportionment component of the AOCPT approach possesses inherent adaptability. Its core relies on the Positive Matrix Factorization (PMF) model, which is fundamentally a data-driven technique. Consequently, when applied to diverse scenarios, such as non-industrial urban areas or winter seasons, the input species and resolved source profiles naturally shift. The AOCPT framework seamlessly integrates

these variations, enabling the precise tracing of dominant oxidation drivers specific to any target environment.

(3) The AOCPT approach focus on relative contribution and sensitivity. The AOCPT approach prioritizes the relative contribution and sensitivity of precursors over absolute concentrations (Zheng et al., 2021; Yang et al., 2024). Even in scenarios with lower absolute AOC levels, such as during winter or in non-industrial areas, the 'bottleneck' driving secondary pollution formation still persists. By utilizing the RIA and REOC metrics, this method effectively identifies these limiting factors within constrained oxidation pathways, enabling the formulation of precise control strategies regardless of the overall pollution magnitude.

We have added a describe on this applicability in line 256-257 of the revised manuscript.

"It is primarily applicable to observation-based diagnoses of complex air pollution in urban environments across different seasons."

Jenkin, M. E., Young, J. C., and Rickard, A. R.: The MCM v3.3.1 degradation scheme for isoprene, Atmos. Chem. Phys., 15, 11433-11459, 10.5194/acp-15-11433-2015, 2015.

Wolfe, G. M., Marvin, M. R., Roberts, S. J., Travis, K. R., and Liao, J.: The Framework for 0-D Atmospheric Modeling (F0AM) v3.1, Geosci. Model Dev., 9, 3309-3319, 10.5194/gmd-9-3309-2016, 2016.

Yan, Y. L., Niu, Y. Y., Duan, X. L., Yue, K., Dong, J. Q., Yang, C., Hu, D. M., Wang, Y. H., Li, J. J., and Peng, L.: Insight into carbonyl source based on improved source apportionment method: Alkene regulate secondary formation, J. Hazard. Mater., 489, 11, 10.1016/j.jhazmat.2025.137649, 2025.

Yang, J., Zeren, Y., Guo, H., Wang, Y., Lyu, X., Zhou, B., Gao, H., Yao, D., Wang, Z., Zhao, S., Li, J., and Zhang, G.: Wintertime ozone surges: The critical role of alkene ozonolysis, Environmental Science and Ecotechnology., 22, 100477, https://doi.org/10.1016/j.ese.2024.100477, 2024.

Zheng, Y., Chen, Q., Cheng, X., Mohr, C., Cai, J., Huang, W., Shrivastava, M., Ye, P., Fu, P., Shi, X., Ge, Y., Liao, K., Miao, R., Qiu, X., Koenig, T. K., and Chen, S.: Precursors and Pathways Leading to Enhanced Secondary Organic Aerosol Formation during Severe Haze Episodes, Environ. Sci. Technol., 55, 15680-15693, 10.1021/acs.est.1c04255, 2021.

2. For REOC parameters, the conversion efficiencies α and β are critical. Please provide the screening criteria for the reaction pathways used and perform a sensitivity analysis to show how variations in these parameters affect the overall AOC conclusions.

Response:

Thank you for your review. We appreciate this critical question regarding the robustness of our metric. We have addressed this comment from screening criteria, uncertainty assessment and sensitivity analysis. The detailed revisions are included in the new Text S4 of the supplementary materials. Accordingly, we have added a cross-reference in the main manuscript (Line 187-189):

"Sensitivity analysis confirms that the reliability of identifying key reactive species was not compromised by parameter uncertainties (detailed in Text S4 and Fig.

S1)."

(1) Screening criteria. The essence of REOC is to indirectly unify the quantification of atmospheric oxidation capacity (AOC) by normalizing various radicals to an equivalent OH· radical generation capacity. As detailed in the manuscript (Section 2.2.2 and 3.2.1), OH· is the primary driver of AOC. Therefore, the screening criteria for reaction pathways were based on the ROx· radical cycling mechanism. We selected pathways that effectively convert intermediate radicals (HO2· and RO2·) back into the OH· pool. Parameters α and β represent the efficiency of these recycling channels.

(2) Uncertainty assessment. We quantified the uncertainty of REOC results based on the propagation of errors from input parameters (measurement errors, kinetic constants, and model-derived results). Consequently, the derived values for α and β are 0.7±0.1 and 4.0±0.8, respectively. This corresponds to an estimated uncertainty of approximately 20%, which falls well within the typical uncertainty range (10% to 30%) for key atmospheric chemical reactions reported in existing studies (Deguillaume et al., 2007).

(3) Sensitivity analysis. We performed a sensitivity test by varying α and β by ±20% (Niu et al., 2024). This range was chosen because it covers the typical uncertainty range of kinetic rate constants (10% to 30%) and measurement errors in atmospheric chemistry (Deguillaume et al., 2007; Niu et al., 2024). The results (Fig. S1) confirm that while absolute values fluctuate, the relative ranking of dominant species (e.g., trans-2-butene) remains unchanged, proving the robustness of our conclusions.

Deguillaume, L., Beekmann, M., and Menut, L.: Bayesian Monte Carlo analysis applied to regional- scale inverse emission modeling for reactive trace gases, #N/A, 112, 13, 10.1029/2006jd007518, 2007.

Niu, Y. Y., Yan, Y. L., Xing, Y. R., Duan, X. L., Yue, K., Dong, J. Q., Hu, D. M., Wang, Y. H., and Peng, L.: Analyzing ozone formation sensitivity in a typical industrial city in China: Implications for effective source control in the chemical transition regime, Sci. Total Environ., 919, 10, 10.1016/j.scitotenv.2024.170559, 2024.

3. Whether the contents in similar color boxes in Part 2 and Part 3 were similarly meaning? if yes, added legend in fig.1. otherwise, distinguish in differ box colors.

Response:

We thank the reviewer for the careful observation regarding the visualization in Figure 1. The boxes in Part 2 and Part 3 belong to different methodological modules (OBM and PMF) and do not represent identical categories. To eliminate any potential ambiguity, we have followed your suggestion and adjusted the color scheme in the revised Figure 1. We now use distinct box colors to visually differentiate the workflows of the OBM module (Part 2) and the PMF module (Part 3). This modification ensures that the distinct logical steps within each module are clearly separated and easily understood.

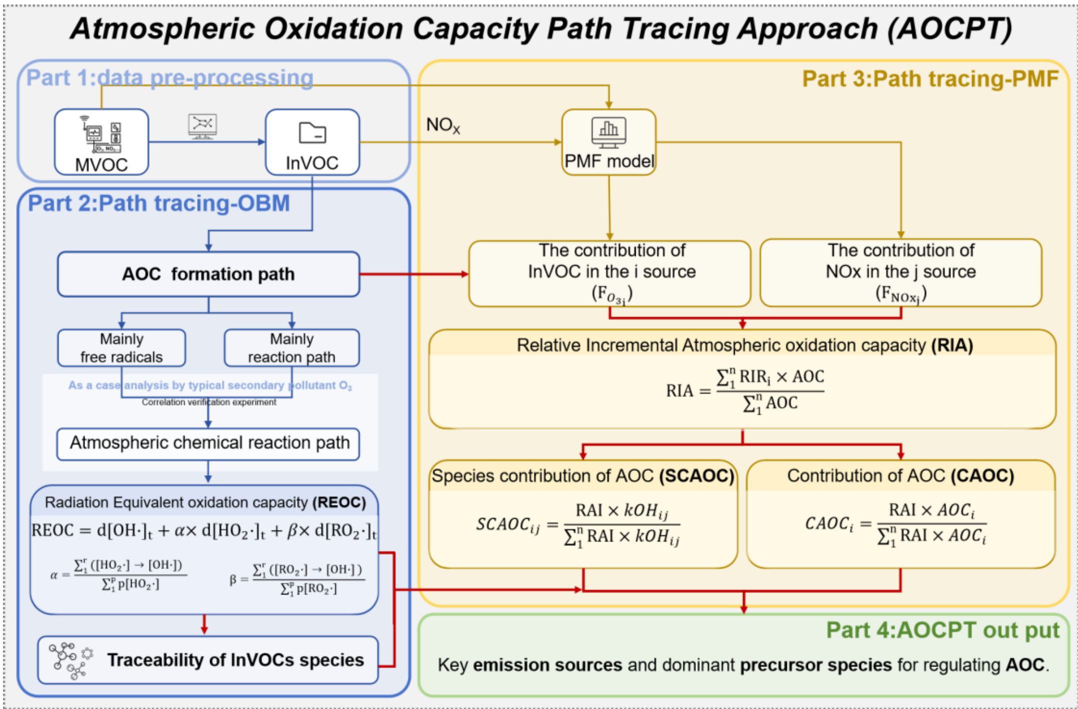

Fig. 1. The workflow of the AOCPT method.

4. The descriptions of Fig. S in manuscript were incorrect, and check them throughout manuscript.

Response:

We sincerely apologize for the oversight regarding the descriptions of Supplementary Figures.

We have conducted a thorough cross-check of the entire manuscript against the supplementary materials. The formatting of these citations throughout the manuscript have been standardized. Additionally, we have corrected all mismatches to ensure that every citation in the main text corresponds accurately to the figures and captions in the Supplementary Information.

5. For better clarity, please label the sub-figures using letters such as (a), (b), etc. Additionally, the bar chart showing the contributions of different oxidizing agent pathways should not be parallel to the time axis. I suggest replacing this bar chart with a pie chart to improve readability.

Response:

We appreciate your helpful suggestion to enhance the visual clarity of the results.

We have redesigned Figure 2 in the revised manuscript to address these points:

(1) We have explicitly labeled the sub-figures as (a) Total, (b) Pollution period, and (c) Clean period for easier referencing.

(2) As suggested, we have incorporated pie charts (donut charts) within each panel to represent the overall contribution proportions of the three major oxidants (OH·, O_3 and NO_3·). This replaces the previous layout and provides a more intuitive visualization of the dominant oxidation pathways under different conditions.

The revisions are as follows:

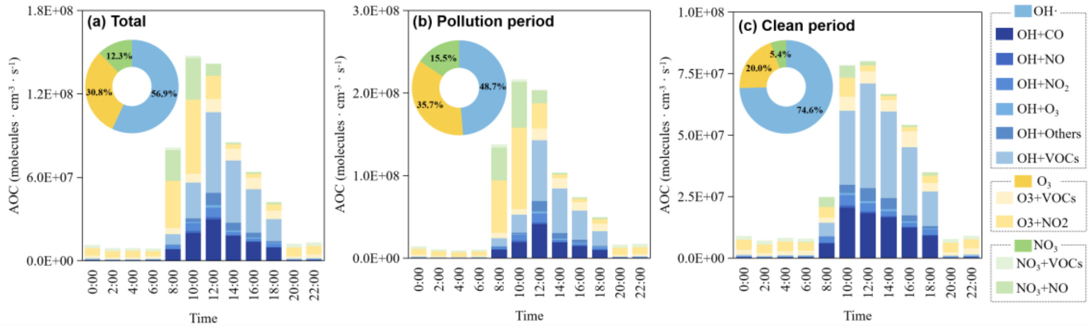

Fig. 2. Diurnal patterns of AOC simulated

6. The manuscript contains an excessive number of figures. I recommend moving some figures to the Supporting Information (SI), such as Fig. 2 and Fig. 4 etc.

Response:

We appreciate your suggestion to streamline the manuscript.

We fully agree that moving descriptive figures to the Supplementary Information improves the readability and flow of the main text.

We have moved the original Figure 2 (Diurnal variations of atmospheric pollutants) and Figure 4 (Diurnal variations of free radicals) to the Supplementary Materials. They are now labeled as Figure S3 and Figure S6, respectively.

Renumbering: Accordingly, we have renumbered all subsequent figures in the main manuscript. For instance, the original Figure 3 (Diurnal patterns of AOC) has become the new Figure 2, and the original Figure 5 (ROx radical cycle) has become the new Figure 3.

Citation Updates: All citations and references to these figures in the main text have been updated to correspond with the new numbering system.

7. The manuscript contains many long and complex sentences, which significantly hinder readability. I suggest the authors revise the text by breaking down complex structures into shorter, more reader-friendly sentences to ensure the scientific findings are communicated clearly.

Response:

We sincerely appreciate your valuable suggestion regarding the readability of the manuscript. We fully agree that clear and concise expression is essential for effectively communicating scientific findings. We have carefully reviewed the entire manuscript and made extensive revisions to simplify sentence structures.

Specifically, we have systematically broken down complex, multi-clause sentences into shorter, independent sentences to improve logical flow and clarity. Special attention was paid to the Abstract and Introduction sections, where the sentence structures were significantly optimized to ensure the research background and objectives are presented clearly. We have also refined the language throughout the Results and Discussion sections to avoid ambiguity.