Response to the Comments of the Reviewers

---For the manuscript "egusphere-2024-1204"

Dear Editor and Reviewers,

We acknowledge the constructive comments and encouragement of the reviewers and are grateful for the efficient service of the editor. Here, we submit our revised manuscript titled "Exploring the Crucial Role of Atmospheric Carbonyl Compounds in Regional Ozone heavy Pollution: Insights from Intensive Field Observations and Observation-based modelling in the Chengdu Plain Urban Agglomeration, China" (Manuscript ID: egusphere-2024-1204), along with a thorough, point-by-point response to each comment raised by the reviewers. The revisions to the manuscript are highlighted in blue text in the attached "Response to the Comments of the Reviewers." Additionally, we have provided a clean version of the revised manuscript as required. We greatly appreciate the reviewers' insightful comments and valuable suggestions, which have significantly improved the quality of our manuscript.

Sincerely yours,

Authors of the manuscript egusphere-2024-1204

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Response to the Reviewer #1

Comment 1: Line 22: change to reflect more precise research questions: i.e., "whether it is the abundance of carbonyls or specific additional chemistry that explains their importance in ozone formation in this context."

Response:

Thank you for your valuable comment. In response, we have revised this sentence to reflect a more precise research question. We now explicitly examine whether it is the abundance of carbonyls or the specific chemical processes involving carbonyls that explain their importance in ozone formation. This revised focus better highlights the core objective of our study, which is to assess the roles of carbonyls in the context of regional ozone pollution.

Lines 22-27：

"To determine whether the impact of carbonyl compounds on regional ozone pollution is driven by their abundance or by specific secondary chemical processes, simultaneous field observations and observation-based modelling of ambient carbonyls were conducted at nine sites within the Chengdu Plain Urban Agglomeration (CPUA), China during August 4-18, 2019, when three episodes of regional heavy ozone pollution occurred across eight cities within CPUA."

Comment 2: Line 27: I don't think you need the second decimal place in the averages and standard deviations reported. Reporting an average of "10.70" when the standard deviation is 4.2 doesn't add anything.

Response: Thank you for your helpful suggestion. We have revised the manuscript to remove the second decimal place in the averages and standard deviations where the precision of the data does not support such fine detail. This change has been applied consistently throughout the manuscript.

Lines 26-27：

“Throughout the study, the total mixing ratios of 15 carbonyls ranged from 10.7 ±4.2 to 35.2±13.4 ppbv.”

Comment 3: Line 39. Answer your more precise research question: is it abundance or additional chemistry that matters?

Response: Thank you for your insightful suggestion. Based on your feedback, we have amended the conclusion to explicitly address the research question. We now emphasize that both the abundance of carbonyls and their specific chemical reactions, such as secondary formation processes, contribute significantly to ozone formation. This revision clarifies that carbonyls play a dual role in ozone pollution, driven not only by their concentrations but also by their chemical reactivity. We believe this update more effectively answers the research question and strengthens the contribution of our study to regional ozone pollution control.

Lines 28-41：

“The spatial distribution reveal that regions with higher concentrations of carbonyl compounds, such as around Chengdu, are also areas with more severe ozone pollution. Both the abundance and the chemical reactivity of carbonyl compounds, especially formaldehyde and acetaldehyde, play crucial roles in ozone formation in the CPUA. On ozone pollution days, carbonyl concentrations significantly increased by 22.8% to 66.2%.While the abundance of carbonyls is an important factor, their significant role in heavy ozone pollution within the CPUA is primarily driven by secondary chemical processes, particularly those involving alkenes and BVOCs. Sites with higher average ozone concentrations during observations were mainly in the VOCs-limited regime, while others were in the transitional regime. Additionally, the mutual transport of carbonyl compounds between cities in the CPUA suggests that regional collaboration is essential to address ozone pollution effectively. These findings offer valuable insights for developing effective strategies to control regional ozone pollution.”

Comment 4: Line 140. change to reflect more precise research question: i.e., "whether it is the abundance of carbonyls or specific additional chemistry that explains their importance in ozone formation in this context."

Response: We appreciate your insightful comments. In response to the suggestion, we have refined the research question to better reflect the key scientific inquiry, which is whether the importance of carbonyl compounds in ozone formation is primarily driven by their abundance or whether additional specific chemical reactions involving these species contribute to their role in ozone production. This modification aligns with the study's objectives to not only quantify the presence of carbonyls but also explore their chemical behavior and reactivity in the context of ozone formation in the CPUA. We believe this refinement provides a more precise focus for the research and better addresses the complexities of photochemical pollution in the region.

Lines 139-145：

"There is still limited understanding of whether the significant roles of carbonyl compounds in ozone formation are primarily due to their abundance or whether specific chemical reactions involving carbonyls drive this process. This study aims to address these gaps by investigating the spatial distribution, sources, and specific chemical pathways of carbonyl compounds across the entire CPUA and assessing their contributions to regional ozone pollution and inter-city air transport mechanisms."

Comment 5: Line 194. Somewhere in this paragraph, or perhaps from line 241, it should be made clear that ketones were not well sampled, so that data for MVK, for instance, is missing.

Response: Thank you for the helpful suggestion. We have clarified in the revised manuscript that ketones, including methyl vinyl ketone (MVK), were not well sampled during the field observations. Consequently, data for MVK and other ketones are missing from the analysis. We have added this information to ensure the methodology is accurately represented.

Lines 240-245：

"It should be noted that while the sampling and analysis method was effective for most carbonyl compounds, ketones, including methyl vinyl ketone (MVK), were not well sampled during the field observations. As a result, data for MVK and other ketones were missing. During the observation period, DNPH cartridges and HPLC analysis technique were used to detect a total of 15 carbonyl compounds (Table S2).”

Comment 6: Line 252. Delete end quotation mark.

Response: Thank you for pointing that out. We have removed the end quotation mark as suggested in the revised manuscript.

Comment 7: Line 307. Please make clear how many carbonyl compounds are in this version of the MCM and how many of those were measured in the study. What values were given to any VOCs, especially carbonyls, not measured?

Response: Thank you for your helpful comment. We have clarified the number of carbonyl compounds included in MCM v3.3.1 and indicated how many of these were measured in our study. Additionally, we have specified that for VOCs, especially carbonyls, which were not measured in our study, the MCM uses estimated values based on emission inventories, literature data, and assumptions from similar species. This ensures the robustness of our model simulations even for unmeasured species.

Lines314-318：

“In this version of the MCM, a total of 19 carbonyl compounds are included, comprising 9 aldehydes and 10 ketones. Of these, 9 carbonyl compounds were measured in this study, including formaldehyde, acetaldehyde, acetone, propionaldehyde, crotonaldehyde, butyraldehyde, isovaleraldehyde, valeraldehyde, and hexaldehyde.”

Lines321-324：

“For VOCs, especially carbonyls, that were not directly measured, the MCM uses estimated values derived from emission inventories, literature data, and assumptions based on similar species to provide estimates for their concentrations and reaction rates.”

Comment 8: Lines 321, 385, 485. Delete space before punctuation mark.

Response: Thank you for your careful review. We have deleted the extra spaces before the punctuation marks in lines 321, 385, and 485, as requested.

Comment 9: Line 388. Please specify if height is above ground level or mean sea level.

Response: Thank you for your suggestion. We have revised the manuscript to specify that the trajectory simulation height is 500 m above ground level (AGL), as per your request.

Lines 392-393：

"A trajectory simulation height of 500 m above ground level (AGL) was selected."

Comment 10: Line 401. Since most VOCs are hydrophobic, I suggest you say "polar volatile organic compounds"

Response: Thank you for your helpful suggestion. We have revised the manuscript to more clearly specify examples of polar volatile organic compounds (VOCs), such as alcohols, aldehydes, ketones, and others, to provide more detail on the types of VOCs involved in ozone formation.

Lines 404-408：

"Although ozone itself is not easily removed by rain, precipitation reduces ozone pollution by washing away its precursors, such as nitrogen oxides (NOx) and polar volatile organic compounds (VOCs), such as aldehydes, ketones, and others, decreasing sunlight exposure, and enhancing atmospheric dispersion."

Comment 12: Line 660. The caption ends unexpectedly. Please define the following acronyms in the caption: ALK, ALE, ACE, ARO, and BVOCs.

Response: Thank you for your suggestion. We have revised the caption to define the acronyms ALK, ALE, ACE, ARO, and BVOCs for clarity, ensuring that readers can easily understand the abbreviations and their corresponding meanings.

Lines 664-666:

“Figure 8. Mean RIRs of formaldehyde, acetaldehyde and acetone to different anthropogenic source VOCs (alkanes (ALK), alkenes (ALE), alkynes(ACE), aromatics (ARO))and biogenic VOCs (BVOCs)at MY, SN, ZY, YA and LS sites on August 11th, 12th and 16th.”

Comment 13: Line 693 or close by. Come back to research gap and address what has been learnt explicitly in terms of that research gap.

Response: Thank you for your helpful suggestion. In response to your comment, we have clarified how this study addresses the research gap regarding the roles of carbonyl compounds in ozone formation. We explicitly discuss how both the abundance and the specific chemical reactions involving carbonyl compounds contribute to ozone pollution in the CPUA, particularly through their secondary formation processes. This new understanding helps fill the existing gap in knowledge and provides valuable insights into the sources and chemical pathways of carbonyls in the region. We believe these clarifications strengthen the overall contribution of our study.

Lines 715-731:

“ Compared to clean days, carbonyl compound concentrations were significantly higher on ozone pollution days, with increases ranging from 22.8% to 66.2%. Between 19.5% and 48.6% of the total volatile organic compound (VOC) ozone formation potential (OFP) was attributed to the 15 carbonyl compounds, highlighting their substantial contribution to ozone formation, particularly formaldehyde and acetaldehyde. While primary emissions are the main sources of these compounds, secondary formation processes contributed over 30% on average to the concentrations of formaldehyde, acetaldehyde, and acetone. Under ozone pollution conditions, the secondary formation concentrations of these three compounds were notably higher than on clean days, with increases of 58.8%, 54.6%, and 57.6%, respectively, emphasizing the critical role of secondary processes in exacerbating regional ozone pollution. OBM modeling revealed that formaldehyde and acetaldehyde primarily originated from the secondary formation of alkenes and

BVOCs, while acetone mainly stemmed from the secondary formation of alkanes. These findings highlight that while the concentration of carbonyl compounds is important, their significant impact on ozone formation is primarily driven by secondary chemistry. Specifically, the secondary formation of these compounds from alkenes and biogenic BVOCs plays a key role in this process."

Comment 14: Line 707. Define FNR again here for those who skip to the conclusions.

Response: Thank you for the suggestion. We have added the definition of FNR (the formaldehyde to NO_2 ratio) in the revised manuscript to ensure clarity for readers who may skip directly to the conclusions.