Itemized Response to Editor's Comments

Ms. Ref. No.: EGUSPHERE-2025-4519 | Measurement report

Title: Measurement report: Characterizing O3-NO_x-VOC sensitivity and O3 formation in a heavily polluted central China megacity using multi-methods during 2019–2021 warm seasons

This work discussed concerns ozone formation within ZhengZhou, China, a mega city with considerable anthropogenic activity. The authors use observations (2019-2021), a box model, CMAQ, and machine learning tools to investigate the emissions sectors and species contributing to ozone during the period.

Unfortunately, this manuscript is rambling and does not present a clear message. "Conclusions" discussed are not traceable, and basic concepts well established in the community about ozone formation are clearly not well understood by the authors. Inadequate discussion of key factors to the analysis, along with generic findings does not lend well to this work, in its current form, being useful to the community and therefore I do not recommend this manuscript for publication in ACP.

Response: Thank you for your careful reading of our paper and the valuable comments and constructive suggestions. Below are the point-to-point responses to all the comments (the comments are marked in black font and the responses are marked in dark blue font). The major changes that have been made according to these responses are marked in yellow in the highlighted copy of the revised manuscript, and our own minor changes are marked in red font. Note that the following line numbers refer to those in the corrected version.

In response to the reviewer's concerns regarding the rambling structure, unclear core message, untraceable conclusions, and misunderstandings of fundamental concepts, we have thoroughly revised the manuscript. Specifically, we have:

- Restructured the manuscript to present a clear, logical narrative, eliminating redundant descriptions and improving overall readability.

- Refined the core message by establishing a coherent "Source–Reactivity–Mechanism" framework that directly links our observational data, source apportionment results, and sensitivity analyses.
- Made all conclusions fully traceable by ensuring each finding is explicitly supported by the corresponding data, figures, tables, or model results presented in the manuscript.
- Strengthened the discussion of fundamental concepts related to ozone formation chemistry, ensuring accurate representation of well-established mechanisms and providing clearer explanations of key processes such as radical chemistry, titration effects, and the non-linear response of ozone to precursor reductions.
- Reorganized the Methods and Results sections to improve coherence, with technical details moved to the Supplementary Information where appropriate.

We hope that these substantial revisions address the reviewer's concerns and that the revised manuscript now meets the standards for publication in ACP. Thank you again for your time and expertise.

Section comments:

Methods: The manuscript uses a variety of models, and methods, many of which are confusing for the reader to understand and follow. The authors need to shorten the observations and methods section (10 pages is excessive), and more succinctly describe the methodology used for this analysis. Make use of supplemental information for details that are not as critical. The paper should convey the main points, the big concepts of this work.

Response: We sincerely appreciate the reviewer’s constructive suggestion regarding the structure and clarity of the Methods section. We agree that a more concise and focused presentation of our methodology will significantly improve the readability of the manuscript. In response, we have performed a comprehensive revision of Section 2: Removal of Redundant Content: We have completely removed the sections related to machine learning (ML) methods. Upon further reflection, we agreed with the reviewer that these methods were not entirely consistent with the observational focus of this report and added unnecessary complexity.

- Streamlining and Restructuring: To reduce the length and improve the flow, we have significantly condensed the descriptions of observations and modeling. Technical details and secondary parameters that are not critical for understanding the main results have been moved to the Supplemental Information.
- Enhancing Methodological Clarity: We have supplemented the descriptions of the Observation-Based Model (OBM) and the Community Multiscale Air Quality (CMAQ) model with key data and essential parameters to ensure the scientific rigor of our analysis while maintaining brevity.
- Standardization: We have carefully reviewed the entire section to unify all abbreviations and terminology, ensuring consistency throughout the manuscript. We believe these changes have made the "Observations and Methods" section much more succinct and better aligned with the core objectives of our work. Thank you for your insightful guidance.

Results:

1. Many of the findings presented in the results section are not groundbreaking, or new, and rely on machine learning techniques which not well described and therefore are questionable at best for accurately accessing relationships between ozone and precursor species.

Response: We sincerely appreciate the reviewer's critical assessment regarding the novelty of our findings and the clarity of our methodology. We have taken these concerns into serious consideration and have implemented substantial revisions to better highlight the unique contributions of this work and to ensure the scientific rigor of our approach.

（1） Regarding the novelty and significance of the findings

While we acknowledge that ozone (O3) studies are extensive, we believe this research provides distinct scientific and practical value through the following aspects:

- Unique and High-Resolution Dataset: Unlike studies based on short-term observations, this work utilizes a continuous, three-year (2019 – 2021) high-resolution online dataset covering 108 VOC species in Zhengzhou, a core megacity in the Central Plains Urban Agglomeration. This long-term dataset provides stronger statistical significance and temporal representation, which is crucial for capturing inter-annual variations and informing stable policy-making.

- Robust Multi-Method Cross-Validation: Rather than relying on a single model, we integrated multiple independent approaches, including OBM-MCM (observation-based), CMAQ-DDM (grid-based), EKMA curves, and Ratio methods. By synthesizing results from tools with different strengths in chemical mechanism description, regional transport, and observational constraints, we reached highly consistent conclusions. This cross-methodological rigor significantly enhances the reliability of our findings beyond that of single-method studies.
- Practical Policy Value: A key "groundbreaking" aspect of this study is the derivation of a specific, quantifiable synergistic reduction ratio (VOCs:NOx = 2.9:1). This provides a science-based, "ready-to-implement" target for local environmental departments to develop forward-looking emission control strategies, bridging the gap between academic discussion and regulatory application.

（2） Regarding the Machine Learning (ML) techniques

We agree with the reviewer that in the context of a mechanistic investigation, the "black-box" nature of certain machine learning techniques may obscure the underlying atmospheric chemistry and complicate the interpretation of precursor relationships.

In response to your suggestion and to ensure the manuscript remains focused on rigorous chemical mechanisms, we have completely removed the machine learning (ML/SHAP) components from the revised manuscript. We have instead strengthened the discussion using traditional, well-established atmospheric chemistry models (as mentioned in Point 1) to provide a more transparent and physically consistent analysis of O3-precursor relationships.

We believe these changes have significantly sharpened the focus and increased the scientific value of the manuscript. Thank you for your guidance.

2. Additionally, the authors mention PM2.5, like a buzz word – the scope of this paper needs to be made smaller and more impactful.

Response: We sincerely appreciate the reviewer's insightful suggestion regarding the scope of our study. We entirely agree that narrowing the focus to O3 and its precursors provides a more concise and coherent narrative, preventing the manuscript from becoming unnecessarily complex and enhancing its overall impact.

In accordance with your recommendation, we have performed the following modifications in the revised manuscript:

（1）Removal of PM2.5 Content: We have removed the descriptions and data related to PM2.5 throughout the manuscript. Specifically, we have deleted approximately seven instances where PM2.5 was mentioned, primarily in the Methodology section and Section 3.1, to ensure the narrative remains focused.

（2）Refined Research Focus: The revised manuscript now focuses exclusively on O3, its precursors, and the associated photochemical mechanisms. This adjustment ensures that the core objectives and scientific findings of the study are emphasized more clearly and effectively.

We believe these changes have significantly streamlined the paper and made the scientific contribution more impactful. Thank you once again for helping us improve the clarity and focus of our work.

3. The units should be mixing ratios when discussing gaseous species, not the variety of units that are currently mentioned in the paper.

Response: We sincerely appreciate the reviewer's constructive suggestion regarding the unification of units. We apologize for the inconsistency in the original manuscript, which indeed created difficulties for the readers.

Following your advice to maintain a single unit throughout the study, we have carefully considered the most appropriate choice. While we acknowledge the reviewer's recommendation to use mixing ratios (ppbv), we have decided to unify all gas concentration units to μg/m³ for the following reasons:

（1） Consistency with Local Standards: The majority of our data analysis and the National Ambient Air Quality Standards (NAAQS) in the study region are based on mass concentrations (μg/m³). Using this unit allows for a more direct comparison with regulatory limits and previous regional studies.

（2） Internal Logic and Calculations: Since the bulk of our original discussion, source apportionment, and health-related impact assessments were conducted using μg/m³, adopting this unit as the standard ensures the internal consistency of our calculations and avoids potential rounding errors or confusion during extensive conversions.

We have now meticulously revised the entire manuscript, including all text, tables, and figures, to ensure that all trace gas concentrations (previously in ppbv or molecules/cm³) are converted and presented consistently in μg/m³. We hope this modification meets with your approval and enhances the clarity of our report.

4. What are the criteria to classify non-polluted, lightly polluted, and moderately polluted days?

Response: We thank the reviewer for this important inquiry regarding the classification of pollution levels. In this study, the classification of non-polluted, lightly polluted, and moderately polluted days was strictly based on the Chinese National Ambient Air Quality Standard (GB 3095-2012) and the associated Technical Regulation on Ambient Air Quality Index (on trial) (HJ 633-2012).

Specifically, the levels are categorized according to the daily maximum 8-hour average (MDA8) concentration of O3 as follows:

- Non-polluted days (Excellent and Good air quality): MDA8 O3 $\leq$ 160 μg/m³.
- Lightly polluted days: 160 μg/m³ $<$ MDA8 O3 $\leq$ 215 μg/m³.
- Moderately polluted days: 215 μg/m³ $<$ MDA8 O3 $\leq$ 265 μg/m³.

We have added these specific criteria to the revised manuscript to provide better clarity for the readers. We appreciate the opportunity to make our methodology more transparent and rigorous.

5. Discussion of the ozone diurnal cycle are not fully accurate, basic knowledge of ozone formation is clearly lacking by the authors. No clear policy relevant message is conveyed – it seems the authors do not have a great handle on the differing results from the different methods used.

Response: We are deeply grateful for the reviewer's critical and constructive feedback. We acknowledge that the previous version of the manuscript was overly descriptive and lacked a sufficiently rigorous exploration of the underlying atmospheric chemistry mechanisms. In response to your concerns, we have fundamentally restructured the logical framework of the study—moving from a descriptive report to a mechanistic analysis—and have thoroughly revised the discussion on O3 formation and policy implications.

The major revisions are summarized as follows:

1. Restructuring the Logical Framework (Source–Reactivity–Mechanism)

To ensure the manuscript is grounded in atmospheric chemistry principles, we have reorganized the discussion to follow a more rigorous scientific logic:

- Observational Evidence (Section 3.1): We have removed the machine learning (ML/SHAP) components to focus on core chemical processes. Critically, we have added a "Weekend Effect" analysis. This serves as a "natural experiment" providing solid, model-independent observational evidence that the study area is in a VOC-limited regime, establishing a robust theoretical foundation for subsequent sensitivity diagnostics.
- Linking Sources to Impact (Section 3.2): We have established a "Mass–Reactivity–Contribution" bridge. Beyond discussing VOC mass (PMF), we now incorporate Ozone Formation Potential (OFP). This explains the mechanistic link between sources and O3 formation: for instance, while traffic and industry contribute significantly to VOC mass, their high content of reactive species (e.g., alkenes and aromatics) leads to an even higher share of OFP (35% for traffic), which justifies the final O3 source apportionment results from CMAQ.
- Mechanism and Sensitivity (Sections 3.3 & 3.4): We merged these sections to

focus on the response of O3 to specific source reductions, using source apportionment results to directly inform the sensitivity analysis.

（2）Integration and Cross-Validation of Methodologies

To address the concern regarding the handling of different methodological results, we have included a Combined Table in Section 3.2. This table provides a horizontal comparison of mass contributions (PMF), reactivity contributions (OFP), and O3 contributions (CMAQ-ISAM). By cross-validating results from these distinct tools, we have significantly enhanced the reliability of our findings and provided a clearer scientific justification for the dominance of specific sectors.

（3）Quantifying Policy-Relevant Conclusions

We have replaced vague suggestions with a concrete, science-based "Chemical Red Line." By synthesizing quantitative data from EKMA isopleths and DDM sensitivity coefficients, we identified a critical VOC/NOx reduction ratio of 2.9:1. We now explicitly state that to achieve a net O3 decrease, VOC emissions must be reduced at a rate at least 2.9 times that of NOx. This provides policymakers with a specific, quantifiable target for effective O3 control.

（4）Systematic Comparison of Sensitivity Methods

To directly address the reviewer's concern regarding the integration of results from different methods, we have added a comprehensive comparative analysis of the ozone sensitivity diagnostic techniques employed in this study. Specifically, we now include a summary table that systematically compares the four main methods used in this work—the VOCs/NOx ratio method, EKMA curves, RIR (OBM-based), and CMAQ-DDM—across key dimensions including their underlying principles, applicability, advantages, limitations, and their specific results in the context of Zhengzhou. This cross-method comparison not only demonstrates the consistency of our core finding (VOC-limited regime) across different diagnostic tools but also highlights the complementary strengths of each approach. The table provides readers with a clear, at-a-glance understanding of why multiple methods were necessary and how their collective application strengthens the robustness of our conclusions.

Method	Main Principle	Advantages	Limitations
Ratio Method (VOCs/NOx)	Uses the concentration ratio of VOCs to NOx to determine ozone formation sensitivity (typically <8-10 indicates VOC-limited, >15-20 indicates NOx-limited).	Simple operation, quick and intuitive; Suitable for preliminary screening using routine monitoring data; Enables rapid identification of sensitivity regimes.	Thresholds based on U.S. experiences (NRC, 1991), lacking regional universality; Ignores reactivity differences among VOC species; Does not account for pollutant dispersion and chemical evolution; Cannot predict future trends (Sistla et al., 2002; Wolff & Korsog, 1992).
EKMA Curves	Uses box models or observation constraints to plot ozone isopleths, visualizing the non-linear response of ozone to precursor reductions; the "ridge line" divides sensitivity regimes.	Intuitively displays non-linear ozone-precursor relationships; Applicable for scenario simulations and policy development; Local thresholds can be adjusted; Clearly distinguishes VOC-limited, NOx-limited, and transition regimes (Dodge, 1977; Chen et al., 2019).	Relies on input parameters (e.g., VOC speciation, meteorology); Does not consider regional transport; Thresholds lack regional universality; Applicable only for daily maximum ozone assessment; Morning VOCs/NOx ratio often not significantly correlated with daily maximum O3 (Sillman, 1999; Shafer & Seinfeld, 1986).
RIR (Relative Incremental Reactivity) (OBM-based)	Uses observation-constrained zero-dimensional photochemical models to simulate the impact of precursor changes on ozone production rates, calculating relative incremental reactivity.	Independent of emission inventories, avoiding inventory uncertainties; Can simulate detailed gas-phase chemical mechanisms (e.g., MCM); Quantitatively identifies key precursors and key VOC species; Suitable for mechanistic studies at point scale (Cardelino & Chameides, 1995).	Requires high time-resolution and high-precision observational data (especially VOC speciation); Results represent only the vicinity of the observation site; Cannot predict long-term trends or regional transport; Chemical mechanisms still involve uncertainties; Cannot directly guide reduction amounts (Russell & Dennis, 2000; Zhao et al., 2020).
CMAQ-DDM (Decoupled Direct Method) (3D	Embeds the decoupled direct method within regional air quality models to quantitatively calculate the sensitivity	Wide spatial coverage, enables assessment of spatial and temporal distribution; Can predict future emission scenarios; Accounts for complete processes	Relies on high-precision emission inventories and meteorological fields; Computationally resource-intensive; Gas-phase chemical mechanisms relatively simplified (to save

model-based)	coefficients of ozone concentrations to precursor emission changes.	including meteorology, transport, and deposition; Results applicable for policy formulation (Dunker et al., 2020; Luecken et al., 2018).	computation); Uncertainties arise from inventories, meteorology, and chemical mechanisms (Kitayama et al., 2019; Liu et al., 2020).

We believe these comprehensive revisions address your concerns regarding the scientific rigor and the clarity of our conclusions. Thank you for pushing us to improve the depth and impact of this work.