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

In "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" Yu et al. investigate the sensitivity of O3 formation in Zhengzhou City between 2019 and 2021 based on VOC in-situ observations, several models and machine learning tools. The authors find that O3 formation in the Chinese megacity is limited by the availability of VOCs and recommend a focus on VOC emission reductions with simultaneous NOx control.

While the investigation of O3 pollution generally remains a highly important topic, I have major concerns regarding the implementation and results presented in this study. The large number of methods, that often seem redundant, the use of many abbreviations (often not defined) and changes between units makes it difficult to follow the line of argument. The lack of presenting NOx measurements and a detailed discussion on the role of NOx in O3 formation makes it additionally challenging to understand how the authors reach their scientific conclusions. Unfortunately, I therefore cannot recommend this manuscript for publication in ACP.

Response: Thank you for your careful reading of our paper and the valuable comments and constructive suggestions. We sincerely appreciate the reviewer's critical assessment, which has helped us identify key areas for improvement. We acknowledge the concerns regarding the large number of seemingly redundant methods, the frequent use of undefined abbreviations, and the lack of clarity in unit conversions, which may have made the line of argument difficult to follow. We also recognize the importance of presenting NOx measurements and providing a detailed discussion on the role of NOx in O3 formation, as these are essential for understanding how we reached our scientific conclusions.

In response to these concerns, we have thoroughly revised the manuscript. 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.

We hope that the revised version now meets the standards for publication in ACP. Thank you again for your time and expertise.

Major Comments:

1. Manuscript type: The manuscript type "Measurement Report" does not seem appropriate to me. A measurement report should "present substantial new results from measurements of atmospheric properties and processes from field and laboratory experiments" (https://www.atmospheric-chemistry-and-physics.net/about/manuscript_types.html). While it can be accompanied by model results, the focus should be on the presentation of a unique dataset rather than a pool of different methods, including modeling and machine learning tools.

Response: We sincerely appreciate the reviewer's critical guidance regarding the definition and scope of a "Measurement Report" in Atmospheric Chemistry and Physics (ACP). We fully agree that the previous version relied too heavily on a "pool of methods," which inadvertently overshadowed the primary value and uniqueness of our observational data.

In light of your suggestions and in strict accordance with ACP's guidelines, we have fundamentally restructured the manuscript to realign its focus on our high-quality, long-term dataset. The specific revisions are summarized below:

(1) Highlighting Substantial New Data in an Understudied Region:

As per the ACP guidelines requiring "substantial new results from measurements," we have emphasized the significance of our 3-year (2019–2021) warm-season dataset of VOCs and O_3 precursors with 1-hour temporal resolution. This dataset represents a rare and substantial record from Zhengzhou, a megacity in Central China that is significantly understudied compared to the North China Plain or the Yangtze River Delta. These high-resolution observations provide essential insights into the inter-annual evolution of urban photochemistry in this region.

(2) Streamlining Methods ("Subtraction" Strategy):

To address the concern regarding methodological redundancy and to refocus on the measurements, we have entirely removed the machine learning (XGBoost/SHAP) sections. We recognized that these "black-box" tools, while innovative, diverted attention away from the empirical evidence provided by the measurements themselves.

(3) Deepening Data Interpretation with New Observational Evidence:

Following the requirement for "preliminary interpretation" within a Measurement Report, we have incorporated new analyses derived directly from the observations:

O_3 Weekend Effect: We added a detailed comparison of VOCs, NOx and O_3 responses between weekdays and weekends. This provides direct, measurement-based evidence of O_3 sensitivity without relying on complex model assumptions.

Chemical Characterization (OFP and Prop-equiv): We now calculate the Ozone Formation Potential (OFP) and Propylene-equivalent concentrations based on the measured VOC species. This allows for a deeper chemical characterization of the dataset, directly linking precursor mass to atmospheric reactivity.

(4) Logical Restructuring:

We have refined the logical flow to follow a natural progression of data interpretation: Observational Characteristics (including the Weekend Effect) → Source Apportionment (Mass vs. Reactivity) → Photochemical Mechanisms (simplified OBM) → Quantitative Control Strategies. In this revised structure, the OBM and CMAQ models are no longer the primary focus; instead, they serve as supporting tools to fulfill the ACP requirement for "discussing the potential significance" of the measured data.

We believe that this restructured version strictly adheres to the spirit of a "Measurement Report" by showcasing a substantial and unique dataset through rigorous, measurement-centric analysis.

2. Number of methods: The authors use a large number of different methods to investigate O3 formation sensitivity. It is not clearly established why all these methods are needed and what their added value is. The questions posed could be answered with a reliable set of in-situ observations and an appropriate model to simulate missing trace gases. Instead, the introduction of all these methods is confusing and makes it difficult to follow the central line of argument.

Response: We sincerely thank the reviewer for this insightful comment. We understand that presenting multiple methodologies could potentially cause confusion if their individual roles and collective value are not clearly articulated. We have carefully reflected on this and have fundamentally restructured the manuscript to present these methods not as a redundant collection, but as a hierarchical, multi-dimensional diagnostic framework.

We believe that the integration of multiple approaches is a key strength of this study. Our rationale for employing this "multi-method" framework is based on the following three aspects:

（1） Cross-verification and Robustness:

As highlighted by recent studies (e.g., Chu et al., 2024), O3 sensitivity analysis is often subject to significant uncertainties stemming from emission inventories, chemical mechanisms, or observation errors. By using independent methods (Observation-based vs. Model-based), we can cross-verify our findings. When different methods point to the same conclusion (in this case, VOC-limited conditions), it greatly enhances the reliability of the results and provides a more solid foundation for policy recommendations.

（2） Hierarchical and Multi-scale Characterization:

O3 formation sensitivity is characterized by complex spatio-temporal dynamics. No single method can capture all dimensions. We have organized our methods into a logical progression:

- Preliminary Diagnosis (Weekend Effect): We have added an analysis of the “weekend effect” as an initial, empirical reality check. It provides direct, measurement-based evidence of how O3 responds to real-world precursor fluctuations.
- Temporal Dynamics (Ratio Method): The VOCs/NOx ratio is used specifically to capture the diurnal (hour-by-hour) evolution of sensitivity, providing a rapid screening of regime shifts during the day.
- Refined Mechanism Analysis (RIR & EKMA): These OBM-based methods are driven by in-situ observations and are independent of emission inventory uncertainties. RIR is used to identify the "key controlling factors" (which specific species to reduce), while EKMA defines the "local reduction thresholds" (the specific proportions needed to reach the O3 ridge line).
- Regional/Spatial Context (CMAQ-DDM): While the above methods are site-specific, the 3D model provides the regional perspective, accounting for transport and meteorology that point-based observations cannot capture.

（3） Policy Support:

For local environmental management, identifying the "what" (key precursors) and "how much" (reduction thresholds) requires multi-dimensional evidence. Our approach provides a comprehensive "toolbox" for stakeholders to develop dynamic, localized control strategies.

To improve clarity, we have added a dedicated table in the revised manuscript that explicitly compares the principles and specific added value of each method:

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 model-based)	Embeds the decoupled direct method within regional air quality models to quantitatively calculate the sensitivity coefficients of ozone concentrations to precursor emission changes.	Wide spatial coverage, enables assessment of spatial and temporal distribution; Can predict future emission scenarios; Accounts for complete processes including meteorology, transport, and deposition; Results applicable for policy formulation (Dunker et al., 2020; Luecken et al., 2018).	Relies on high-precision emission inventories and meteorological fields; Computationally resource-intensive; Gas-phase chemical mechanisms relatively simplified (to save computation); Uncertainties arise from inventories, meteorology, and chemical mechanisms (Kitayama et al., 2019; Liu et al., 2020).

In the revised manuscript, we have also improved the transitions between these sections to ensure the "central line of argument" is logical and easy to follow. We believe these changes clarify that these methods are complementary and essential for a robust assessment of O3 sensitivity in a complex urban environment.

3. Measurements: From the results section, I understand that besides VOCs, measurements of NOx and O3 are available. However, there are no details presented in the methods section.

Response: We would like to express our sincere gratitude to the reviewer for pointing out the omission of measurement details for NOx and O3. This information is indeed essential for a complete understanding of our data foundation. Following your suggestion, we have added a description of these measurements in the revised "Methods" section and provided comprehensive technical details, including instrument specifications and QA/QC protocols, in the Supplementary Materials.

The key details regarding these measurements are as follows:

(1) Data Source and Co-location:

The NOx and O3 data were obtained from the Zhengzhou National Air Quality Monitoring Station. To ensure high data comparability, this station is co-located within the same monitoring area as our VOC sampling and meteorological observation sites. Furthermore, one of our co-authors, Minghao Yuan, who is a staff member at this monitoring station, directly supervised the data acquisition, ensuring the highest level of data integrity.

(2) Instrumentation and Standards:

All gaseous pollutants were measured using high-precision analyzers compliant with China's National Environmental Protection Standards (HJ 193-2013):

NOx was measured using a chemiluminescence analyzer (e.g., Thermo Fisher Scientific 42i). O3 was measured using a UV photometric analyzer (e.g., Thermo Fisher Scientific 49i).

(3) QA/QC and Maintenance:

The monitoring process strictly adhered to the Technical Specifications for Operation and Quality Control of Ambient Air Quality Continuous Automated Monitoring System (HJ 817-2018).

- Professional Maintenance: Routine maintenance, including daily zero/span checks and weekly precision audits, was performed by qualified third-party professional institutions.
- Data Validation: Multi-point linear calibrations were conducted monthly to ensure measurement accuracy. Any data affected by power fluctuations or localized site interference were strictly screened and excluded.

4. NOx: Besides VOCs, Nitrogen Oxides are important precursors to tropospheric O3. However, the role of NOx seems to be mostly neglected in this study. A detailed description and discussion of the role of NOx are missing and I wonder how the authors reached their conclusions on O3 formation sensitivity, without accounting for NOx. E.g. the authors state that chemistry is VOC-limited in Zhengzhou, but suggest that VOC control is more important than NOx. VOC-limited chemistry is characterized by a large excess of NOx, which requires drastic emission cuts to improve long-term air quality.

Response: We have carefully revised the manuscript to include a more comprehensive analysis of NOx and to clarify our control strategy logic. Our detailed responses are as follows:

(1) Clarification of NOx Inclusion in Sensitivity Models

We would like to clarify that the role of NOx was fully considered in our sensitivity simulations. The Observation-Based Model (OBM) was constrained by high-resolution, hourly observed NOx data. The conclusions regarding O3 formation sensitivity (e.g., Relative Incremental Reactivity (RIR), EKMA, and DDM results) were derived based on the current high-titration environment. The results indicated that while both precursors are present, the O3 production rate is currently much more sensitive to changes in VOCs than to NOx in the urban area of Zhengzhou.

(2) Scientific Basis for Prioritizing VOCs Controls (Short-term vs. Long-term)

We fully concur with the reviewer's assessment that VOCs-limited regimes are typically characterized by an excess of NO. In Zhengzhou, the extremely high NO concentrations exert a strong "titration effect" (NO +O3→NO2 + O2), which locally suppresses O3 levels.

- Short-term Strategy: Under these strong VOC-limited conditions, moderate reductions in NOx can lead to an "O3 disbenefit"—where the weakened titration effect causes O3 concentrations to rise. Therefore, to achieve rapid compliance with air quality standards in the short term, prioritizing VOCs reductions is the most direct and effective approach to suppress O3 peaks.
- Long-term Strategy: We completely agree with the reviewer that long-term, sustainable air quality improvement requires deep and synergistic cuts in NOx emissions. Only through substantial NOx reduction can the chemical regime eventually transition across the "ridgeline" into a NOx-limited regime. We have added a discussion in the "Policy Implications" section to emphasize that VOCs control is a current priority, while synergistic NOx reduction remains the ultimate long-term goal.

(3) Evidence from the "Weekend Effect" Analysis

To further address the reviewer's concern, we have added a detailed analysis of the "Weekend Effect" in the revised manuscript. The observed increase in O3 concentrations during weekends, despite lower NOx emissions from reduced heavy-duty traffic, provides empirical evidence of the strong NOx titration effect and the VOCs-limited nature of the study area. This analysis helps to validate the sensitivity results obtained from our models.

We have incorporated these detailed descriptions and discussions into the revised manuscript. We believe these additions clarify the indispensable role of NOx in our study and strengthen the logical consistency of our proposed control strategies.

5. Correlation analysis: The presentation of correlations between different parameters in Section 3.1.1 seems random and does not follow a clear strategy, e.g. hypothesis – method – result – discussion. The set of in-situ observations is much more powerful than this: I recommend presenting trace gas levels (and if possible a longer time series), the characteristics of each season, diurnal cycles and the weekend effect for a sensitivity analysis. The application of machine learning tools is not necessary here or needs to be better justified.

Response: We sincerely thank the reviewer for these constructive comments and the strategic suggestions for restructuring our manuscript. We have carefully revised Section 3.1 and the overall analysis framework to better utilize the richness of our three-year in-situ dataset and to ensure a clearer scientific logic. The specific modifications are as follows:

（1） Restructuring the logic of Section 3.1

We have reorganized Section 3.1 to follow a "macro-to-micro" strategy, moving from an overall assessment of pollution trends to specific chemical mechanisms. The new structure follows a clear logic of: General Overview – Diurnal Evolution – Empirical Sensitivity Evidence.

- Section 3.1.1 (Macro Overview): We now present the full 2019–2021 warm season (May–September) time series. We have added a comparative analysis between non-polluted and polluted days to establish the links between meteorological drivers (e.g., temperature, humidity, and radiation) and ozone accumulation. This addresses the reviewer's concern regarding the previously "random" presentation of correlations.
- Section 3.1.2 (Dynamic Diurnal Evolution): We merged the previous diurnal analysis into this subsection. By comparing the diurnal cycles of O3, NOx, and VOCs under different pollution levels, we highlight the "chemical fingerprints" of ozone episodes, such as the rapid accumulation of NO in the morning and its titration effects at night.

2. Deepening the analysis of observational data (Weekend Effect)

Following the reviewer's suggestion to better exploit the in-situ observations, we have added a new section (Section 3.1.3) focusing on the "Weekend Effect."

We compared the concentrations of NOx, VOCs, and O3 between weekdays and weekends. Our statistical findings show that while NOx levels decrease during weekends, O3 concentrations remain high or even increase. This "weekend effect" serves as robust, purely observational evidence that the study area is in a VOCs-limited regime. This provides a solid foundation for the subsequent source apportionment and OFP calculations without relying on black-box models.

3. Addressing the necessity of Machine Learning

We agree with the reviewer that for a "Measurement Report," the focus should remain on chemical mechanisms and observational facts. Therefore, we have removed the machine learning tools (XGBoost and SHAP analysis) from the manuscript. This removal allows the paper to be more concise and ensures that the conclusions are directly supported by the three-year high-resolution monitoring data.

We believe these changes significantly improve the logical flow and the scientific weight of the observational analysis. Again, we thank the reviewer for guiding us toward a more rigorous presentation of our findings.

6. Abbreviations: Many abbreviations are used in this manuscript, and they are often not defined upon first use, which makes it difficult to follow. It is further concerning that the authors are in some cases not consistent with the abbreviations, e.g. “OBM” is an “observation-based model” in Line 41 and an “Ozone Box Model” in Line 128.

Response: We sincerely apologize for the oversight regarding the inconsistent and undefined abbreviations in our original manuscript. We appreciate the reviewer's meticulous attention to detail, which is crucial for the clarity and professional standing of our work.

In response to your suggestion, we have conducted a comprehensive review of the entire manuscript and implemented the following improvements:

(1) Standardization and Consistency: We have meticulously checked all abbreviations to ensure they are defined upon their first mention. Specifically, the term "OBM" has been unified as "Observation-Based Model" throughout the text (e.g., corrected in Line 128) to eliminate any ambiguity.

(2) Global Correction: Every abbreviation used in the manuscript, including those in figures and tables, has been cross-verified for consistency in both formatting and meaning.

(3) Addition of an Abbreviation List: To further enhance readability and provide a convenient reference for readers, we have added a comprehensive "List of Abbreviations" . This table summarizes all technical terms and their corresponding full names used in the study.

We are truly sorry for any confusion caused by our previous presentation and hope that these systematic corrections ensure the manuscript is now clear and easy to follow.

7. Units: Many different units for trace gases are used throughout the text, including ppbv, ug/m3 and molecules/cm3. This makes it difficult to compare trace gas levels and I recommend choosing one unit (preferably mixing ratios) and using it throughout

the entire manuscript.

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.

8. PM2.5: Why is PM2.5 relevant to this study? I recommend focusing on O3 and its precursors to avoid overloading this study.

Response: We genuinely appreciate the reviewer's insightful suggestion regarding the scope of our study. We agree that focusing on O3 and its precursors provides a more concise and coherent narrative, preventing the manuscript from becoming unnecessarily complex.

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

(1) Removal of PM2.5 Content: We have removed the descriptions and data related to PM2.5 throughout the manuscript. This includes the approximately seven instances where PM2.5 was mentioned, primarily in the Methodology section and Section 3.1.

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

We believe these changes have significantly streamlined the paper and thank you for helping us improve its clarity and focus.

Minor comments:

- 33 f.: This sounds like VOCs increase in response to O3 increases, while VOCs are precursors to O3.

34 f.: Do these values refer to VOC or O3 concentrations?

Response: We appreciate the reviewer's insightful comments regarding the causal relationship between VOCs and ozone. We have revised the text to clarify that VOCs, as precursors, contribute to the varying levels of ozone pollution. We also explicitly stated that the numerical values provided refer to the mass concentrations of VOCs.

The revised sentence in the manuscript now reads:

"Mean VOC mass concentrations were found to be higher during more severe ozone episodes, with values of 84.7±51.0, 96.6±53.4, and 105.3±59.4 μg/m³ for non-polluted, mildly polluted, and moderately polluted periods, respectively, reflecting the role of these precursors in ozone formation."

- 37: Please define abbreviations upon first use.

Response: We thank the reviewer for this suggestion. The full names for CMAQ (Community Multiscale Air Quality) and PMF (Positive Matrix Factorization) have been provided at their first mention in the revised manuscript. We have also carefully checked the text to ensure all other abbreviations are properly defined upon initial use.

- 39: What is meant by "ozone emissions"? Ozone is not emitted but formed photochemically.

We are grateful to the reviewer for pointing out this oversight. We fully agree that ozone is a secondary pollutant formed through photochemical reactions rather than being directly emitted. To rectify this, we have replaced "ozone emissions" with "ozone formation" throughout the revised manuscript to ensure scientific accuracy.

- 46: What's the "ratio method"?

Response: We thank the reviewer for pointing out the lack of clarity regarding the "ratio method." We have now explicitly defined this term in the revised manuscript. Specifically, the "ratio method" refers to the diagnostic approach of using the ratio of precursor concentrations (VOCs/NOx) to determine the sensitivity of ozone formation. We have also ensured that the definition is clearly presented upon its first mention to avoid any ambiguity.

- 47: If ozone generation is limited by VOCs, it is highly important to control NOx. Of course, it remains important to reduce VOCs simultaneously, but long-term air quality improvements can only be reached through NOx reductions in that case.

Response: We sincerely appreciate the reviewer's insightful comment regarding the long-term importance of NO_x reduction. We fully agree that NO_x control is the fundamental driver for sustained, long-term air quality improvements on a regional scale.

However, in the specific urban context of Zhengzhou, our findings indicate that the city is currently located in a strongly VOC-limited regime. Under such conditions, prioritizing the synergistic reduction of VOCs is more direct and effective for controlling O_3 peak concentrations and reducing the number of exceedance days in the short term. To reflect this perspective, we have added a discussion in the revised manuscript to clarify the distinction between long-term NO_x-focused goals and short-term, VOC-oriented mitigation strategies for peak ozone control.

- 55 ff.: Several things are missing in the introduction, i.a. how O3 is formed from its precursors and particularly what the role of NOx is.

Response: We appreciate the reviewer's constructive suggestion. In the revised manuscript, we have expanded the first paragraph of the Introduction to provide a concise yet comprehensive description of the O_3 photochemical formation mechanism. Specifically, we have incorporated the radical cycle involving VOCs, NO_x, and OH radicals. Furthermore, we have clarified the dual role of NO_x in ozone chemistry, emphasizing both the NO_2 photolysis cycle, which leads to O_3 production, and the NO titration effect, which acts as a sink for O_3. We believe these additions provide the necessary theoretical foundation for the subsequent discussion.

- 65 ff.: Are the authors saying that they are the first to investigate O3 formation from increasing anthropogenic sources?

Response: We apologize for the imprecise expression in the original manuscript, which may have led to a misunderstanding regarding the novelty of our work. We did not intend to claim that we are the first to investigate the general relationship between anthropogenic sources and O3 formation.

Instead, our goal was to provide a systematic investigation specifically focused on Zhengzhou—a representative megacity experiencing rapid urbanization and significant shifts in emission characteristics in recent years. In the revised version, we have adjusted the tone to emphasize that this study offers a "comprehensive assessment through integrated multi-model analysis and systematic monitoring" tailored to this specific region and period. We have revised the relevant sentences to more accurately reflect our contribution.

Thank you for your valuable feedback, which helped us present our findings more humbly and precisely.

- 76 f.: This sounds like the range of VOC mixing ratios in China is 27 – 92 ppbv.

Response: We sincerely thank the reviewer for pointing out this ambiguity. We apologize for the imprecise phrasing in the original manuscript, which may have inadvertently suggested that the VOC mixing ratios across the entire country were confined to a narrow range.

Our intention was to highlight the significant spatial variability of VOC concentrations across different Chinese cities. To clarify this, we have revised the sentence to specify that these values represent specific observations from different regions. The revised text now reads: "In China, VOC pollution exhibits complex spatial and temporal patterns; for instance, previous studies have reported average summertime VOC concentrations ranging from 27.0 ppbv in Nanjing to 92.0 ppbv in Tianjin."

We have updated this section to ensure the description is more accurate and clear. Thank you for your careful reading.

- 81 ff.: This section is difficult to follow due to the jumps between countries and continents.

Response: We sincerely apologize for the lack of clarity in the original geographical transitions. Following the reviewer's constructive suggestion, we have reorganized this section to improve the logical flow. We now follow a 'from-global-to-regional' and 'from-characteristic-to-source' structure. Specifically, we first summarize the global diversity in VOC compositions and sources, and then transition to a detailed discussion of the complex patterns within China. This ensures a smoother transition before identifying the specific research gaps that this study aims to address.

This paragraph has been revised and rewritten as follows.Recent research has advanced our understanding of VOCs, key precursors to ozone. As revealed by global monitoring data, there are substantial geographical differences in the chemical composition and source profiles of VOCs. Globally, VOC signatures are highly region-specific. For instance, alkanes dominate the VOC pool in Colorado, USA (>80%), whereas oxygenated VOCs (OVOCs) prevail in Athens, Greece (Abeleira et al., 2017; Kaltsonoudis et al., 2016). Similarly, source contributions shift from LPG and solvents in Paris to biomass burning in Punjab, India (Baudic et al., 2016; Pallavi et al., 2019). Within China, VOC pollution manifests through complex spatiotemporal patterns, with concentrations varying widely—from 27.0 ppbv in Nanjing to 92.0 ppbv in Tianjin (An et al., 2017; Han et al., 2015). While fossil fuel combustion and solvent use are the primary drivers in the North China Plain, the petrochemical industry remains a dominant contributor in the Yangtze River Delta (Mozaffar et al., 2020).

- 83: Is BB the major VOC source throughout the entire year?

Response: We sincerely thank the reviewer for this insightful question, which has helped us improve the temporal precision of our description.

We agree that the dominance of biomass burning (BB) as a VOC source is highly seasonal rather than year-round. The study cited (Pallavi et al., 2019) was conducted during the winter months, a period characterized by intensive crop residue burning and increased heating demands in the Punjab region.

- 93 ff.: Are the authors talking about concentrations, emissions, formation rates or sensitivities?

Response: We thank the reviewer for identifying this ambiguity. In Lines 93 ff., we are primarily discussing O_3–NOx–VOCs sensitivity (i.e., the response of O_3 concentrations to changes in precursor levels).

We have clarified the text to state that while precursor emissions and concentrations are the drivers, and formation rates are the kinetic outputs, the focus of this section is on the diagnostic methods (like EKMA and OBM) used to determine the sensitivity regime (VOC-limited vs. NO_x-limited). The revised text now explicitly uses the O_3–NOx–VOCs sensitivity to avoid confusion

- 115 ff.: Why not use a set of in-situ observations?

Response: The reviewer's point is well-taken. In fact, this entire study is fundamentally built upon a comprehensive 3-year (2019-2021) dataset of high-resolution in-situ observations (including 108 VOC species, O_3, NOx, and meteorological parameters).

We chose the multi-method approach (OBM, PMF, and CMAQ) precisely to maximize the diagnostic value of these in-situ observations:

- OBM: Directly utilizes in-situ concentrations to calculate real-time radical budgets and O_3 production rates.
- PMF: Uses the observed chemical fingerprints to trace the physical sources of VOCs.
- Statistical Analysis: We also included direct analysis of observed trends, ratios, and correlations (e.g., Section 3.1).

By combining these, we provide a more robust chemical interpretation than what could be achieved by simple statistical descriptions of in-situ data alone. We have updated the text in Line 115 to more clearly emphasize that our analysis is observation-driven."

- 128: In the Abstract the authors state the OBM to be an observation-based model.

Response: It was my oversight; it is indeed "an observation-based model" here, and it has been corrected.

- 188: How were other trace gases and meteo parameters measured?

Response: We appreciate the reviewer's inquiry regarding the measurement methods for trace gases and meteorological parameters. In response, we have added detailed descriptions in the revised manuscript. Specifically, these data were obtained from the Zhengzhou National Air Quality Monitoring Station. To ensure high data comparability, this station is co-located within the same monitoring area as our VOC sampling and meteorological observation sites. Furthermore, one of our co-authors, Minghao Yuan, who is a professional staff member at this monitoring station, directly supervised the data acquisition process. This involvement ensured the highest level of data integrity and quality control. We hope these clarifications address your concerns.

- 215: More details on the OBM are required.

242: More details are needed on the WRF/CMAQ model.

Response: We have added more comprehensive details for both models. For the OBM, we have clarified the chemical constraints (MCM v3.3.1) and the 1-hour time step. For the WRF/CMAQ, we added a new table in the Supplementary Information (Table S1) detailing the nested grid settings (36/12/4/1 km) and physical schemes to ensure model stability.

- 223: The reaction of OH and NO2 does not destroy O3 but limits its formation. It should therefore be accounted for in Equation (3), rather than (4).

Response: The reviewer is absolutely correct. The reaction of OH and NO_2 is a termination step that removes precursors and radicals, thereby limiting O_3 formation rather than directly destroying O_3 molecules. We have relocated this term from the destruction equation (Eq. 4) to the discussion of formation limitation in Section 2.2.1 and updated the equations accordingly to ensure kinetic rigor.

- 248 ff.: What are all these abbreviations: FNL, SAPRC-99, AERO6, IC/BC, MEIC, REAS2?

Response: We have provided the full names for all technical abbreviations upon their first mention in the revised manuscript to ensure clarity for the readers.

FNL: Final Operational Global Analysis (NCEP)

SAPRC-99: Statewide Air Pollution Research Center 1999 mechanism

AERO6: Sixth-generation CMAQ aerosol module

IC/BC: Initial Conditions and Boundary Conditions

MEIC: Multi-resolution Emission Inventory for China

REAS2: Regional Emission inventory in ASia version 2

- 262 f.: What are first- and second-order sensitivities of O3?

265 ff.: What exactly do these equations show?

Response: We have clarified the physical meaning of the DDM equations:
First-order sensitivities (S_V,S_N): Represent the local linear response (the slope) of O_3 concentration to changes in VOCs and NOx emissions.
Second-order sensitivities (S_{VV},S_{NN},S_{VN}): Capture the non-linearity of the O_3 response surface. For instance, S_{VV} describes the curvature of the O_3-VOCs relationship, which is critical for understanding why the effectiveness of emission controls changes as

reductions intensify.

Equations (5)-(9) collectively allow us to reconstruct the Taylor expansion of the O_3 response, providing a robust diagnostic of the sensitivity regime.

- 277: Why is PM2.5 needed in this study?

Response: We appreciate the reviewer's insightful suggestion. Upon careful consideration, we agree that the inclusion of $PM_{2.5}$ data might deviate from the primary focus of this study. To enhance the clarity of the manuscript and maintain a more concentrated discussion on the research theme, we have removed all $PM_{2.5}$ related content in the revised version. We believe this modification makes the study more concise and better aligned with our core objectives. Thank you for your professional guidance.

- 283: Why would the model be better at simulating emitted species?

Response: Primary species (e.g., SO_2 or NOx) primarily depend on the accuracy of emission inventories and transport/dispersion, which are relatively linear. In contrast, secondary pollutants like O_3 involve complex, non-linear chemical transformations and radical cycling. The accumulation of uncertainties in reaction mechanisms, precursor levels, and meteorological feedbacks typically makes secondary species more challenging to simulate than primary ones.

- 284: Only a small fraction of NO2 is emitted directly, most is formed photochemically from NO.

Response: The reviewer is correct. NO is indeed the dominant primary emission, and most NO_2 is formed via NO + O_3. We have revised the text to clarify that the model performs better for NOx as a primary precursor group compared to the purely secondary O_3, as the former is more directly constrained by the emission inventory.

- 319: What’s MDL?

Response: MDL stands for Method Detection Limit, defined as the lowest concentration of a substance that can be identified with 99% confidence to be greater than zero. We have added the full name to the text.

- 348: Why exactly is machine learning needed in this study?

Response: Upon reflection and in response to the reviewer's concern, we have realized that the machine learning component, while providing some quantitative weightings, introduced unnecessary complexity and was not as physically intuitive as our OBM and CMAQ results. To make this Measurement Report more focused on chemical mechanisms and observational data, we have entirely removed the machine learning section from the revised manuscript.

- 425 / Fig. 1: Why is a smoothing applied? What exactly does it involve? Why is the time series not just averaged to the desired resolution?

Response: Savitzky-Golay smoothing was applied in Fig. 1 solely for visualization purposes to reduce high-frequency noise and better reveal the seasonal and inter-annual patterns of pollutants. We have clarified this in the figure caption.

- 426 ff.: All three numbers are the same. How exactly are the pollution levels defined?

Response: We apologize for the clerical error. The levels are defined based on China's National Ambient Air Quality Standard (GB 3095-2012) for MDA8 O_3: Non-polluted ($\leq$160μg/m^3), Lightly polluted (160<MDA8$\leq$215μg/m^3), and Moderately polluted (>215μg/m^3). The text has been corrected.

- 432: What exactly do the percentage values relate to? If it's years, the time period is too short for a trend analysis.

Response: The percentage values refer to the frequency of exceedance days within the sampling period of each year. We agree that a 3-year period is insufficient for a climatological 'trend' analysis. We have replaced 'downward trend' with 'inter-annual variation' to accurately reflect the year-to-year changes in the proportion of polluted days during our study.

- 437: Why is O3 positively correlated with wind speed? Usually, higher wind speeds lead to less accumulation?

Response: In Zhengzhou, the positive correlation between O_3 and wind speed is primarily due to: (1) Regional transport, where strong winds bring O_3 or its precursors from upwind polluted areas; and (2) Meteorological coupling, as higher wind speeds during the warm season in this region often coincide with clear skies and intense solar radiation, which are the primary drivers for O_3 formation.

- 438: Because H2O contributes to O3 loss? These correlations need to be discussed in more detail.

Response: The negative correlation with RH is twofold: (1) Chemical loss: High water vapor concentrations enhance the sink of O_3 through the reaction $O^1D + H_2O \rightarrow 2OH$; (2) Radiation attenuation: High RH is typically associated with increased cloud cover, which attenuates the UV radiation required for photolysis. We have expanded this discussion in the revised Section 3.1.1.

- 476 / Fig. 2: Why is half the figure upside down?

Response: This figure was part of the SHAP interpretability analysis for the machine learning model. As we have removed the entire machine learning section (as explained in the General Response), this figure has been deleted from the revised manuscript.

- 482 f.: It should be specified what is meant by “affecting boundary layer structure” – the current term is very generic.

494: HO2 can be lost on aerosol surfaces, which inhibits O3 formation (opposite effect!)

Response: We are grateful to the reviewer for pointing out the importance of HO_2 heterogeneous loss on aerosol surfaces and its inhibitory effect on O_3 formation. We acknowledge that the previous description was imprecise. In accordance with the reviewer's suggestions and to improve the overall quality of the paper, we have removed the machine learning-related content and the corresponding discussion in this part. This revision helps to avoid potential inaccuracies and ensures that the manuscript remains focused on the core findings. Thank you for your professional and rigorous guidance.

- 522 ff.: I cannot follow this logic. NO is lower for high O3 days because (a) O3 generation is VOC-limited or because (b) of the titration effect close to NOx sources (NO + O3 --> NO2 + O2)

Response: The lower NO concentration on high O_3 days is primarily attributed to the titration effect ($NO + O_3 \rightarrow NO_2 + O_2$). Under high O_3 conditions, NO is rapidly consumed and converted to NO_2. This explains why we observe a negative correlation between NO and O_3 levels in an urban environment like Zhengzhou. The text has been revised to clarify this chemical feedback.

- 556 ff.: It is important to control NOx when chemistry is VOC-limited.

Response: We thank the reviewer for this important comment. We fully agree that controlling NOx emissions when the atmospheric chemistry is in a VOC-limited regime is indeed critical. In such regimes, reducing NOx without corresponding reductions in VOCs may actually increase O3 levels due to reduced titration, as we have discussed in relation to the "ozone disbenefit" concept. This highlights the necessity of coordinated emission control strategies. We have now emphasized this point in the revised manuscript to better guide policy implications. Thank you again for your valuable insight.

- 559 ff: What exactly are these different phases? Is titration meant by suppression?

Response: We thank the reviewer for this clarifying question. By "different phases," we refer to the distinct diurnal stages of O_3 behavior: (1) the suppression phase (P1) during midnight and early morning, where O_3 is suppressed by fresh NO emissions via titration ($NO + O_3 \rightarrow NO_2 + O_2$); (2) the photochemical generation phase (P2) during daytime, where O_3 accumulates due to VOC/NO_x reactions under sunlight; and (3) the titration phase (P3) prior to the evening peak, where O_3 is again consumed by reaction with NO from rush-hour emissions. Titration is indeed a form of suppression, but we have delineated these phases to capture the full diurnal cycle.

- 571: Is there a specific reason to investigate midnight concentrations? Maybe the analysis should be limited to daylight values.

Response: While midnight concentrations provide insights into the residual background and nocturnal NOx titration, we agree that the daylight period is more critical for O_3 formation analysis. We have shifted the primary focus of our radical and reactivity discussions to the peak photochemical hours.

- 652: These sources emit both VOCs and NOx.

656 ff.: How exactly were these factors identified? Why are there six factors? Additional explanations are needed here.

Response: The 6-factor solution was selected based on both statistical criteria (Q/Q(exp)) ratio, stable BS and DISP results) and physical interpretability. While we acknowledge these sources also emit NOx, the PMF analysis is inherently based on VOC species fingerprints. We have added a more detailed justification for the 6-factor selection in Section 2.3.2 and Section 3.2.1.

- 696 ff. / Fig. 6: There does not seem to be a relevant difference between the three cases. What's the uncertainty? Are the differences even significant?

Response: We thank the reviewer for this insightful comment. Although the overall VOC composition in a region is relatively stable, Figure 6 reveals that as pollution levels increase, the contributions from biogenic sources, as well as anthropogenic sources such as vehicles and combustion, exhibit an upward trend. This pattern provides valuable insights for ozone pollution control strategies.

- 706 ff.: Please provide an explanation for speculations.

Response: We have replaced the term 'speculation' with a more detailed kinetic explanation. During O_3 pollution periods, enhanced solar radiation and radical levels (OH) significantly accelerate the oxidation of highly reactive aromatics from solvent use. We have provided evidence by comparing the ratios of reactive species (e.g., xylenes) to stable tracers (e.g., ethane), which shows a clear decrease during peak hours, confirming their rapid chemical consumption.

- 799 ff.: Sillman et al. suggested the HCHO to NO2 ratio for O3 sensitivity analysis.

Response: We thank the reviewer for the suggestion regarding the HCHO/NO_2 indicator. We fully acknowledge the importance of the HCHO/NO_2 ratio in diagnosing ozone sensitivity, as highlighted in classic studies such as Sillman (1995). It should be noted that in the present study, we did not conduct field observations of HCHO, nor did we use satellite-based HCHO data products. Therefore, our ozone sensitivity analysis primarily relies on ground-based VOCs/NOx ratios and diagnostic methods such as RIR and EKMA. In future work, we plan to incorporate HCHO observations or satellite-retrieved HCHO data to further validate and extend the findings of this study.

- 803: What is MEM?

827: What is RIR?

Response: We have clarified these abbreviations: MEM stands for the Municipal Environmental Monitoring station, and RIR stands for Relative Incremental Reactivity. We have ensured they are defined upon first mention.

- 944: It is not clear why the slope of the ridge could indicate the ratio at which VOCs and NOx need to decline. Wouldn't it be important to reduce NOx as quickly as possible to move towards NOx limited chemistry?

Response: This is a critical point for policy formulation. In VOC-limited urban areas like Zhengzhou, prematurely reducing NOx without concurrent VOCs control can lead to an 'Ozone Disbenefit' (an increase in O_3 due to weakened titration). The 'ridge line' in the EKMA plot represents the transition boundary; its slope (2.9:1) provides the optimal 'pathway' for synergistic reduction. This ratio ensures that O_3 levels decline steadily while moving the system toward a NOx-limited regime without causing transient spikes.

- 961: What is meant by "high-resolution observations" – the hourly measurements?

Response: By 'high-resolution observations,' we refer to both the hourly temporal resolution of the measurements and the comprehensive suite of chemical species (108 VOC species) monitored. We have revised the text to 'hourly, multi-species observations' to be more precise.