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 manuscript investigates O_3–NOx–VOC sensitivity and O_3 formation mechanisms in Zhengzhou (2019–2021) using a combination of online VOC measurements, OBM, CMAQ-DDM, source apportionment, PMF, and machine-learning (ML)/SHAP interpretation. While the dataset is valuable and the research direction is meaningful, the manuscript suffers from inconsistent methodology, unclear descriptions of model configurations, uncertainties and machine learning, no comparisons between different analytical models for the O_3 formation mechanism, and very vague data interpretation. The manuscript is long and unreadable. Therefore, I suggest the manuscript be rejected.

Response: We sincerely thank you for your careful reading of our manuscript and for providing valuable comments and constructive suggestions. In response to the concerns raised—including inconsistent methodology, unclear descriptions of model configurations, lack of uncertainty analysis, vague machine learning interpretation, absence of cross-model comparisons regarding O_3 formation mechanisms, and ambiguous data interpretation—we have thoroughly revised the manuscript.

Below are our point-by-point responses to all comments (reviewer comments are in black font; our responses are in dark blue font). Major revisions made in response to these comments are highlighted in yellow in the marked-up version of the revised manuscript. Minor revisions made at our own initiative are indicated in red font. Please note that line numbers referenced below correspond to those in the revised manuscript.

Major Comment:

1. In Section 3, “Results and Discussion”, there is a substantial focus on O3 source apportionment (CMAQ) and VOCs source apportionment (PMF). Unfortunately, how these contents are linked to the research question “O3-NOx-VOC sensitivity” is weak. For example, the authors claim that traffic and industry dominate both O3 and VOCs. But there is no justification for “X% of O3 from traffic” and “how O3 responds if traffic NOx/VOCs are reduced”.

In addition, there is no cross-method comparison. A combined table is highly recommended to show the section contributions across PMF, CMAQ-DDM, and OBM RIR/EKMA. As a result, the manuscript reads like a report by stacking results (sensitivity diagnostics + VOC and O3 source apportionment + ML/SHAP), but with limited discussion.

Response: We sincerely appreciate the reviewer's critical feedback regarding the logical flow and the "stacking" of results. We agree that a stronger connection between source apportionment and sensitivity analysis is essential to elevate the manuscript's academic depth. Following your constructive suggestions, we have performed a fundamental restructuring of Section 3 to establish a clear "Source–Reactivity–Mechanism" narrative. Our revisions are detailed as follows:

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

To transform the manuscript from a descriptive report into a mechanistic study, we have reorganized the discussion to follow a more rigorous scientific logic:

Observation as the Foundation (Section 3.1): We have removed the machine learning (ML/SHAP) components to reduce complexity and focus on atmospheric chemistry. Crucially, we added a "Weekend Effect" analysis as direct observational evidence. This "natural experiment" provides solid, model-independent proof that the

study area is in a VOC-limited regime, serving as the basis for subsequent sensitivity diagnostics.

Linking Sources to Impact (Section 3.2): We established a "Mass–Reactivity–Contribution" bridge. Previously, Section 3.2 only discussed VOC mass; we now incorporate Ozone Formation Potential (OFP) as a vital link. This explains why traffic and industry dominateO3 formation: while they contribute significantly to VOC mass (PMF), their high concentration of reactive species (e.g., alkenes and aromatics) leads to an even higher share of OFP (e.g., 35% for traffic). This justifies the finalO3 source apportionment results from CMAQ.

Sensitivity as the Core (Sections 3.3 & 3.4): These sections have been merged to avoid result-stacking. We now use the source apportionment results to inform the sensitivity analysis, directly addressing "howO3 responds" to specific source reductions.

（2）Cross-Method Comparison and Validation

We have included a Combined Table in Section 3.2 as recommended. This table horizontally aligns the mass contributions (PMF), reactivity contributions (OFP), and O3 contributions (CMAQ-ISAM). By cross-validating results from these different tools, we have significantly enhanced the reliability of our conclusions and provided a clearer justification for the dominance of specific sectors.

（3） Quantifying Policy-Relevant Information

Regarding the reviewer's concern about "howO3 responds," we have replaced vague suggestions with a specific "Chemical Red Line." By extracting quantitative data from the EKMA isopleths and DDM sensitivity coefficients, we identified a critical VOC/NOx reduction ratio of 2.9:1. We clarify that to achieve a netO3 decrease, VOC emissions must be reduced at a rate at least 2.9 times that of NOx. This provides policymakers with a concrete, science-based target.

We believe this restructured logic significantly strengthens the connection between our findings and addresses the reviewer's concerns regarding the depth of discussion.

2. The CMAQ simulation suggests that transportation and industry dominate MDA8 O_3 contributions, while the PMF result indicates that vehicle, solvent, and industrial sources contribute most VOCs. The current discussion is very vague: “transportation should be prioritized,” “more aggressive control is required,” etc. However, what is the take-home message for policy translation? There are no recommended emission-reduction scenarios (e.g. -30% traffic VOCs, -30% industrial NOx, different VOC/NOx ratios by sector) and no quantitative estimate of the expected O3 under those scenarios.

Response: We sincerely appreciate the reviewer's suggestion regarding the need for more concrete policy-relevant insights. We agree that translating scientific findings into actionable management strategies is crucial.

In response to your concerns, while we have not added new hypothetical emission-reduction scenarios (such as -30% reduction simulations), we have significantly refined the discussion in Section 3.2 and Section 4 to provide more specific and quantitative "take-home messages" based on our existing data-driven results. Our reasoning and the subsequent improvements are as follows:

(1) Quantitative Prioritization via the "Mass-Reactivity-Contribution" Chain

Instead of relying on vague recommendations, we now utilize the re-evaluated logic in Section 3.2 to provide a semi-quantitative basis for policy. By linking PMF (mass), OFP (reactivity), and CMAQ (contribution), we explicitly demonstrate why the transportation sector is the primary target. For instance, the fact that traffic VOCs account for the largest share of OFP (35%)—coupled with its high NOx emissions—provides a data-backed justification for prioritized control, rather than just a general suggestion.

(2) Utilizing Sensitivity Coefficients (RIR) as Quantitative Indicators

We have enhanced the discussion of the Relative Incremental Reactivity (RIR) and EKMA results in Section 3.3. These results already provide the quantitative sensitivity ofO3 to its precursors (i.e., theO3 response per unit change in precursors). By emphasizing these coefficients, we provide a quantitative measure of reduction benefits without the need for additional, and potentially uncertain, scenario simulations. This aligns with our focus on a "data-driven" investigation rather than a purely model-oriented sensitivity study.

(3) Clarification of Research Scope and Focus

We have clarified in the manuscript that this study is designed as a detailed diagnostic investigation based on high-resolution observations and source apportionment. Our goal is to provide a robust physical and chemical diagnosis of currentO3 pollution. We believe that identifying the "key drivers" through cross-method verification provides a more reliable foundation for policy-making in this specific study area than simulating hypothetical scenarios that may involve high degrees of uncertainty in emission inventory scaling.

(4) Refined Policy Recommendations

The revised Section 4 now provides more granular advice. For example, instead of "prioritizing transportation," we now specify that control efforts should focus on high-reactivity VOC species identified in the traffic and industrial sectors (e.g., alkenes and aromatics), as these are proven to be the most "cost-effective" targets based on our OFP and RIR analysis.

We believe these revisions make the policy implications of our work much clearer and more grounded in the presented data. Thank you for pushing us to sharpen the practical value of our research.

3. Machine-learning setup and data leakage risk are not clearly addressed. The authors use XGBoost and RF with grid search and cross-validation (CV), and report training/test metrics in Table S4. However, essential methodological details are missing. How are training and test sets defined—random split or chronological split

for this time-series dataset? What CV scheme is used (k-fold, blocked time-series CV)? Does CV account for temporal ordering?

We would like to express our sincere gratitude to the reviewer for these highly professional and insightful comments regarding our machine learning (ML) methodology. Your concerns regarding the potential for data leakage in time-series datasets and the necessity of a robust cross-validation (CV) scheme are technically well-founded and crucial for ensuring the reliability of such models.

After careful consideration of your feedback and re-evaluating the core objectives of this manuscript as a "Measurement Report," we have decided to remove the machine learning (XGBoost and Random Forest) analysis from the revised manuscript. Our decision is based on the following considerations:

(1) Refocusing on Observational Data and Chemical Mechanisms: As a "Measurement Report," the primary value of this study lies in its high-resolution observational dataset and the underlying atmospheric chemical processes. We found that while the ML models provided supplementary quantitative insights, they functioned as a "black box" that was less intuitive for explaining specific chemical mechanisms compared to the OBM, PMF, and OFP analyses.

(2) Streamlining the Manuscript Logic: In line with the reviewer's suggestion to clarify the narrative, removing the ML section allows the manuscript to be more concise and focused. This "subtractive" approach eliminates the methodological uncertainties and potential risks associated with ML setups (such as the data leakage you correctly identified), thereby strengthening the overall transparency and physical interpretability of our findings.

(3) Prioritizing Physico-chemical Diagnosis: By focusing on the "Mass-Reactivity-Contribution" bridge and the OBM-based sensitivity analysis, we ensure that our conclusions are grounded in robust, physically-based atmospheric chemistry rather than purely statistical associations.

We believe that this major revision significantly improves the clarity and focus of the manuscript, ensuring it aligns more closely with the expectations for an atmospheric measurement investigation. Thank you again for your rigorous review, which helped us identify this opportunity to refine our work.

4. What is the inherent relationship between the VOCs/NOx ratio method for determining O3 sensitivity, modelling results from OBM and CMAQ, and radical budgets?

Response: We sincerely appreciate the reviewer's insightful comment. This question touches upon the theoretical core of our study—the consistency between microscopic chemical mechanisms and macroscopic atmospheric observations.

In response, we have substantially restructured the manuscript by merging the original Section 3.3 (Radical chemistry) and Section 3.4 (O3 sensitivity) into a single, integrated discussion. This allows us to explicitly demonstrate the inherent relationships through a "Diagnostic Chain" moving from "Preconditions → Internal Mechanisms → Local Diagnostics → Regional Validation."

The specific relationships are articulated as follows:

（1） Radical Budgets: The Microscopic "Engine" (The Mechanistic Foundation)

The radical budget is the fundamental driver of O3 formation. Our analysis shows that radical loss is dominated by the OH + NO2 reaction ($L_N > L_R$), which directly dictates the chemical regime. This microscopic imbalance—where NO2 outcompetes VOCs for OH radicals—is the primary reason why the system is sensitive to VOC increments.

2. VOCs/NOx Ratio: The Macro-scale "Indicator" (The Environmental Background)

The VOCs/NOx ratio represents the atmospheric chemical environment that sets the stage for radical competition. The observed low ratio (< 10 ppbC/ppbv) provides the macro-scale context for the NOx-saturated conditions found in the radical budget. It serves as a preliminary proxy that is consistent with the more detailed kinetic analysis.

3. OBM (RIR/EKMA): The Local "Scalpel" (The Quantitative Diagnostic)

The OBM translates the complex radical cycling (captured via MCM mechanism) into quantitative sensitivity metrics (RIR and EKMA). It acts as a local diagnostic tool that answers how the O3 "engine" responds to specific precursor changes based on the in-situ radical cycling efficiency.

4. CMAQ (DDM): The Regional "Laboratory" (The Spatial Validation)

While the above methods focus on local chemistry, the CMAQ-DDM provides a 3D perspective considering transport and regional emissions. The consistency between CMAQ results and our OBM/radical budget findings confirms that the radical-driven VOC-limited regime observed at the monitoring site is representative of the broader urban area of Zhengzhou.

Summary of Integration:

By restructuring Section 3.3, we emphasize that these four methods are not independent metrics but a coherent evidence chain. The consensus among the initial conditions (VOCs/NOx ratio), internal kinetics (radical budgets), local response (OBM), and regional manifestation (CMAQ) robustly supports our conclusion regarding the VOC-limited regime and the proposed 2.9:1 reduction ratio.

We hope these clarifications and the integrated section better address the reviewer's concern. The revised text can be found in the updated Section 3.3.

5. How do the results of XGBoost relate to those of other methods? Why is XGBoost analysis not mentioned at all in the Section 4 Summary and Conclusions? How do the authors come up with the claim that the ML method should be advised in the future in the subsection Limitations and future research directions in Line 986?

Response: We are extremely grateful to the reviewer for these critical observations. Your assessment that the XGBoost analysis felt disconnected from the core chemical mechanisms and was not adequately integrated into the conclusions is very accurate.

Upon careful reflection and in alignment with your previous comments regarding "data leakage" and methodological clarity, we have decided to completely remove the machine learning (ML) component (including XGBoost and Random Forest) from the revised manuscript. Our reasoning and the subsequent changes are as follows:

（1）Resolving the Logical Disconnect:

We acknowledge that the ML results in the previous version acted as a "separate layer" that did not harmonize well with the traditional physico-chemical models (OBM and PMF). As you noted, this lack of integration led to a narrative where the ML analysis seemed isolated. By removing this section, we have eliminated this logical "two-skin" problem, ensuring that the manuscript remains strictly focused on atmospheric chemical diagnosis and source apportionment.

（2）Adhering to the "Measurement Report" Focus:

The primary value of this study lies in its high-resolution observational data and the mechanistic insights derived from established chemical models. Removing the "black-box" ML analysis allows us to emphasize the empirical evidence and chemical pathways, which are the core requirements of an ACP Measurement Report.

（3）Correcting the Conclusions and Future Research Directions:

In response to your specific question regarding Line 986, we have deleted the claim recommending ML methods in the "Limitations and future research" section. We have also ensured that the Summary and Conclusions (Section 4) are now entirely consistent with the remaining data-driven and mechanism-based results.

We believe these "subtractive" revisions have significantly strengthened the internal logic and professional focus of the paper. We sincerely thank the reviewer for identifying these inconsistencies, which allowed us to refine the manuscript into a more coherent and rigorous scientific report.

6. The role of biogenic VOCs is mentioned but not fully clarified in terms of

O3 formation and control. Biogenic VOCs are explicitly identified as a separate PMF factor with isoprene as tracer, and OBM RIR shows that biogenic VOCs have non-negligible reactivity, especially on polluted days. Emissions used in CMAQ also include biogenic VOCs via MEGAN. On the one hand, the authors claim that the contribution of biogenic sources to VOC is small (Line 724). On the other hand, they claim that the contribution of biogenic VOCs to local O3 is high (Lines 840-850). So, I wonder what the overall role of biogenic VOCs in the O3–NOx–VOC sensitivity and O3 formation mechanism is.

Response: We sincerely thank the reviewer for this insightful observation. The perceived contradiction regarding the "small mass contribution" versus "high ozone contribution" of biogenic VOCs (BVOCs) is a critical point that requires further clarification. We have thoroughly revised the manuscript to address the "Mass vs. Reactivity" paradox and to better elucidate the role of BVOCs in local photochemistry. Our response and the corresponding revisions are detailed below:

（1） Resolving the "Mass vs. Reactivity" Paradox

We acknowledge that the previous version did not sufficiently distinguish between mass-based and reactivity-based contributions. While our PMF results indicate that BVOCs (primarily isoprene) contribute a relatively small fraction to the total VOC mass concentration (Line 724)—largely due to their extremely short chemical lifetimes and rapid consumption—their impact on ozone formation is disproportionately large.

In the revised manuscript, we have introduced the Propylene-equivalent concentration (Prop-equiv) and Ozone Formation Potential (OFP) metrics to quantify this effect. Our new analysis demonstrates that although isoprene ranks low in mass, it exhibits the highest Prop-equiv concentration among all sources due to its exceptionally high OH radical reactivity (k_{OH}). This high reactivity explains why BVOCs are identified as major contributors to localO3 in our OBM and CMAQ simulations (Lines 840-850).

（2） The Overall Role of BVOCs in O3 Formation and Sensitivity

We have added a new discussion in Section 3.3 to clarify the role of BVOCs in theO3–NOx–VOC sensitivity:

- As a "Photochemical Fuel": BVOCs provide highly reactive substrates that significantly accelerate the photochemical cycle, especially during the high-temperature and high-radiation periods typical of polluted days.
- As a "Sensitivity Shifter": The presence of strong biogenic reactivity ensures that the atmosphere remains highly reactive even when anthropogenic VOCs (AVOCs) are relatively low. This background reactivity makes localO3 production more sensitive to further reductions in AVOCs, particularly high-reactivity species from industrial and transportation sources.

（3） Clarification and Consistency in the Manuscript

To ensure logical consistency, we have revised the language throughout the text:

- In Section 3.2 (formerly Line 724), we now specify that "BVOCs have a limited contribution to the total VOC mass burden, but play a dominant role in chemical reactivity."
- We have included a comparison in the revised manuscript (Table/Figure) showing the contrast between mass percentage and Prop-equiv percentage for different sources to provide a visual confirmation of this "low abundance, high activity" phenomenon.
- By removing the machine learning components as suggested in your other comments, we have dedicated more space to a rigorous chemical diagnosis of these biogenic-anthropogenic interactions.

We believe these revisions provide a much clearer and more scientifically robust explanation of the biogenic contribution to ozone formation in the study area. We are grateful for the opportunity to refine this aspect of our work.

Minor Comment：

1. The period simulated by the CMAQ model was not mentioned in the methodology.

We apologize for the omission of the simulation period in the initial manuscript and thank the reviewer for this careful observation. We have now added the specific details to the Methodology section (Section 2.3).

The CMAQ simulation was conducted for June 2019. The selection of this specific period and year is based on the following considerations:

（1） Representativeness of Peak Pollution: June was chosen because it represents the most severe ozone (O3) pollution period in the study area (Zhengzhou). Simulating this window allows for a more robust analysis of the chemical mechanisms under peak pollution conditions.

（2） Reliability and Consistency: 2019 was selected as the base year for the simulation. This year has been extensively validated and used as a benchmark in several peer-reviewed studies previously published by our research group. Utilizing this well-established baseline ensures the credibility and consistency of our modeling results with existing regional emission and meteorological datasets.

In the revised manuscript, we have updated the "Model Configuration" part of the Methodology section as follows:

"The CMAQ model simulations were performed for June 2019, which coincides with the peak of O3 pollution in Zhengzhou. This year was selected as the base year to maintain consistency with our group's previously validated regional studies, ensuring the reliability of the emission inventory and meteorological inputs."

We hope this addition clarifies the scope of our modeling work.

2. What is the rationale for studying warm seasons? Could you provide any justification and supporting references?

Response: We sincerely appreciate the reviewer's constructive suggestion regarding the temporal scope of our study. The rationale for focusing on the warm season (May to September) is based on the following considerations:

（1） Peak Period ofO3 Pollution in Zhengzhou

The selection of May to September is primarily driven by the seasonal characteristics of air quality in Zhengzhou. Statistical monitoring data and our previous research indicate that O3 exceedances and high-concentration events are heavily concentrated during these five months, which coincide with high solar radiation and temperatures—key drivers for photochemical reactions.

（2） Foundation of Previous Research

This study builds upon a series of investigations conducted by our research group in the North China Plain. Our prior published works have consistently identified May–September as the most critical window for O3 mitigation in Zhengzhou. Focusing on this period ensures that our findings are highly relevant to the most severe pollution episodes, providing a solid scientific basis for the current analysis.

3. Categorization of Pollution Levels

The core objective of this study is to explore the dynamic relationship between VOCs andO3 under varying atmospheric conditions. By focusing on the high-frequencyO3 season, we can effectively categorize the data into different pollution levels (e.g., clean vs. polluted days). This allows for a more nuanced understanding of how precursor sensitivity shifts as pollution intensifies, which is a central theme throughout the manuscript.

We have incorporated these justifications and the suggested references into the Introduction section as follows:

"Although the Central Plains urban cluster centered on Zhengzhou has achieved significant progress in controlling primary pollutants, the paradoxical situation of persistently rising ozone levels still exists in this area, particularly characterized by

the high frequency of O3 pollution episodes from May to September (Yu et al., 2020 and 2021). This persistent challenge necessitates an urgent investigation into its formation mechanisms during these critical periods (Jia et al., 2024; Li et al., 2020; Min et al., 2022; Yu et al., 2021)."

We hope these clarifications and the added references sufficiently address the reviewer's concern.

3. Lines 141-143: Could you provide any reference for the study city of Zhengzhou?

Response: We thank the reviewer for this reminder. The air quality ranking mentioned in the manuscript is based on the official statistics released by the Ministry of Ecology and Environment (MEE) of the People's Republic of China. We have added the formal citation for this report.

Additionally, to provide a more comprehensive academic context for Zhengzhou's severe pollution status, we have also cited peer-reviewed literature characterizing the historical and persistent air quality challenges in this region (e.g., Wang et al., 2021; Yu et al., 2021).

The text has been updated as follows:

Zhengzhou... faces severe air pollution, with its air quality ranking among the bottom twenty of 168 major cities in China from January to September 2024 (MEE, 2024; Wang et al., 2021).

（4）Lines 212-215: “PO3S(X) and PO3S (X-DX) refer to the simulated O3 yields…” Are you sure “yield” is the right terminology here? Why does the author later state that “The net O3 production rate (PO3S)” in Lines 215-216?

Response: We apologize for the imprecise terminology. "Yield" has been replaced with "net O_3 production rate" ($P(O_3)$, ppbv/h) throughout the manuscript to maintain consistency with the OBM results and Equation (2).

（5）The CMAQ result shows transportation can contribute 64% to O3 (Fig.4), but the PMF result shows vehicles contribute only 31% to VOCs. This apparent

discrepancy needs justification. Presumably, VOCs and NO_x emissions from transportation are equally important for O_3 formation. Therefore, the role of NOx emissions needs to be discussed.

Response: The discrepancy arises because PMF measures mass contribution, while CMAQ calculates O3 impact. As shown in the newly added OFP and Prop-equiv analysis, transportation-derived VOCs have disproportionately high reactivity. Furthermore, transportation is a major source of NOx. In the VOC-limited regime of Zhengzhou, the synergistic impact of NOx and reactive VOCs from traffic leads to the higher O_3 contribution (64%).

（6）Why does Table S5 show a negative correlation (Kendall's, -0.305) between VOCs and O3, while the RIR indicates a positive correlation (Fig.9)? Shouldn't this discrepancy require some explanations?

We appreciate the reviewer's insightful observation regarding the apparent discrepancy between the negative statistical correlation (Table S5) and the positive RIR values (Fig. 9). This distinction is indeed critical for a nuanced understanding of atmospheric photochemistry. We have added a detailed explanation in the revised manuscript to clarify this point.

Response: Our response and the rationale for this phenomenon are summarized below:

（1） Statistical Correlation (Concentration) vs. Chemical Sensitivity (Production Rate)

The negative Kendall's correlation in Table S5 reflects the relationship between the observed concentrations of VOCs and O3, which are influenced by the complex interplay of physical transport, boundary layer dynamics, and chemical transformation. In contrast, the RIR (Fig. 9) represents the chemical sensitivity of the O3 production rate to its precursors. It specifically answers how the net photochemical formation of O3 changes in response to a perturbation in precursor levels, independent of physical dilution.

（2） The Influence of Boundary Layer Dynamics (Physical Factor)

The negative correlation in concentration is largely driven by the diurnal evolution of the planetary boundary layer (PBL). During the early morning, the shallow PBL traps primary emissions, leading to peak VOC concentrations, while O3 remains low due to the lack of sunlight and NO titration. Conversely, in the afternoon, the rising PBL height dilutes VOC concentrations, while intense solar radiation triggers rapid photochemical O3 formation, leading to an O3 peak. This "seesaw" effect inherently results in a negative statistical correlation between their ambient concentrations.

（3） Photochemical Consumption of Precursors (Chemical Factor)

During periods of high O3 production, the concentration of OH radicals typically reaches its peak. These radicals rapidly consume VOCs through oxidation. Consequently, the period of maximum O3 production often coincides with a significant depletion of VOCs. This chemical "sink" further contributes to the observed negative correlation between the two species in ambient air.

（4） Consistency with the VOC-limited Regime

The positive RIR values indicate that the study area is in a VOC-limited regime, where increasing VOCs enhances O3 formation potential. The negative correlation does not contradict this; rather, it highlights that the observed concentrations are dominated by physical processes and consumption, while the RIR captures the underlying chemical driving force.

We believe these clarifications address the reviewer's concern and strengthen the interpretation of our results.

（7）&(8) Table S4: The rationale for selecting XGBoost over RF is well justified.

A strong positive correlation between O3 and alkenes is observed in SHAP (Fig.2), whereas Spearman's analysis reveals the opposite relationship (Table S6, -0.054). Please standardise the terminology for “olefins” (Fig.2) or “Alkene” (Table S6)

Response: We appreciate the reviewer's insightful observation. 1. Regarding the discrepancy between SHAP and Spearman's results: To ensure the internal consistency and maintain the focus of a Measurement Report, we have decided to entirely remove the Machine Learning (ML) section (including the XGBoost model and SHAP analysis). We agree that the contradiction between SHAP and statistical analysis highlights the uncertainties of the ML model in this context. Removing this section allows the manuscript to focus on more robust observational and OBM-RIR results. 2. Regarding terminology standardization: We have standardized the terminology to "Alkene" throughout the manuscript and supplementary materials, replacing "olefins" as suggested. Thank you for your constructive guidance, which has helped us simplify and strengthen the manuscript.

（9）Line 427: “160 160 μg/m³ and 160 μg/m³ are categorised as light pollution and moderate pollution”? Could you please carefully check if this is CORRECT?

Response: We apologize for the typo. The text has been corrected according to the GB 3095-2012 standard: MDA8 O_3 > 160 μg/m³ is light pollution, and > 215 μg/m³ is moderate-to-severe pollution.

（10）What are “AVOCs”, “ALKA”, “ALKE”, “ARO”? What is the relationship between them? Which subsets of compounds belong to AVOCs? Why is there no further discussion of the contribution and sensitivity of VOCs from different sources to O3?

Response: We appreciate the opportunity to clarify these definitions and the logical structure of our analysis. 1. Definitions and Relationships: We have added explicit definitions in the manuscript. AVOCs refers to Anthropogenic Volatile Organic Compounds, which in this study is the sum of three chemical groups: ALKA (Alkanes), ALKE (Alkenes), and ARO (Aromatics). 2. Discussion on VOC Contribution to O3: To better address the contribution and sensitivity of different VOC groups toO3 formation, we have added the Ozone Formation Potential (OFP) analysis in Section 3.2. This addition bridges the gap between VOC sources andO3

production, resulting in a more coherent logical flow: VOC Source Apportionment → OFP Analysis →O3 Sensitivity (RIR analysis). This sequence provides a comprehensive evaluation of how various VOC precursors and their sources contribute to ozone formation. The corresponding sections and figures have been updated to reflect these clarifications. Thank you for your constructive feedback.

Technical Comment:

1. The font is too small to read.

Line 351: What is the full name of "XGBoost"?

Line 386: Should it be "SHAP" instead of "Shapley"?

Response: As detailed in our general response, to streamline the manuscript and focus on the core chemical diagnostics, we have completely removed the machine learning and SHAP analysis sections (including the former Figure 2). Therefore, these specific terminological and formatting issues are no longer applicable.

Table S3: What do "DISP" and "BS" mean? What is the meaning of BS mapping＜ 80%?

Response: We have added full descriptions for these PMF diagnostic terms in the Supplemental Information. BS stands for Bootstrap and DISP stands for Displacement. A BS mapping < 80% (specifically for certain factors) indicates potential rotational ambiguity or instability in those factors; however, we have retained the 6-factor solution because it provided the most physically meaningful source profiles and passed the DISP error estimation without any factor swaps. We have clarified this in the revised Table S3 caption.

S3: A full description needs to be provided for "E/X" in the manuscript for the first time and figure captions.

Response: Thank you for your valuable suggestion. We have added the full description of "E/X" at its first mention in the manuscript and in the corresponding

figure captions. Specifically, E and X denote ethylbenzene and m,p-xylene, respectively. The E/X ratio is employed as a diagnostic tracer to estimate the photochemical age of air masses, based on the differing reaction rates of these species with OH radicals. We appreciate your careful reading.

Line 712: “Zhengzhou comprises vehicle emissions (31%), solvent use (24%), and industrial processes (21%)”. But in Table S8, the corresponding values are 32.4%, 24.8% and 18.3%.

Response: We sincerely apologize for this discrepancy. The values in Table S8 were incorrectly based on a different timeframe (May 2019–September 2021). We have updated Table S8 to ensure full consistency with the results reported in the main text. Thank you for your meticulous review.

Lines 1135-1137: Make sure the font style is consistent throughout.

Please be consistent in the use of subscripts and full names or abbreviations for proper nouns.

Response: We have thoroughly revised the manuscript to ensure consistent font styles (including Lines 1135-1137). A comprehensive check was conducted to standardize the use of subscripts (e.g., O3, NOx) and the consistent application of abbreviations and full names for all proper nouns and chemical species