

Response to Reviewer #2

Comment: *The manuscript entitled “Impact of Primarily Emitted Oxygenated Volatile Organic Compounds (OVOCs) on Ozone Formation in the Yangtze River Delta Region” presents a timely and valuable contribution to understanding the role of OVOCs in radical chemistry and ozone production. By integrating source-resolved OVOC emission profiles into the CMAQ model and evaluating them against observations during two typical pollution episodes, the study provides new insights into the contributions of primary OVOCs to HO₂ production and O₃ formation. Overall, the manuscript is well structured, the topic is highly relevant to ACP, and the results are scientifically meaningful. The use of source-resolved emission profiles and process-based analysis represents a methodological advancement with clear implications for regional air quality management. I believe the study has strong potential for publication after revisions. The specific comments are as follows.*

Response: We thank the reviewer for the positive and constructive feedback on our study. The comments have greatly helped improve the clarity and overall quality of the manuscript. In response to the reviewer’s suggestions, we have: (1) explicitly articulated the scientific gaps addressed by this study; (2) elaborated on the methodology and uncertainties associated with the emission profiles; (3) refined the description of observational data processing; and (4) clarified concepts related to radical chemistry. Detailed responses to each comment are provided below. The reviewer’s comments are shown in black italics, our responses are in blue, and revisions in the manuscript are highlighted in red.

Comment: *1. While the Introduction section provides a comprehensive overview of OVOC chemistry, emission uncertainties, and model limitations, the scientific gap addressed by the present study is not explicitly articulated. The manuscript would benefit from clearly stating (1) what aspects of primary OVOC contributions to HO₂ and O₃ formation remain unresolved in current literature. (2) How existing CTM/box model approaches fall short in quantifying emitted vs. secondary OVOC pathways. (3) Why a sector-resolved emission inventory is essential for addressing these limitations. More explicit formulation of these open questions at the end of the Introduction would help readers better understand the novelty and motivation of the study.*

Response: Thank you for this valuable comment. To emphasize the gaps in quantitatively assessing the contributions of primary emissions to OVOC concentrations and influences in radical chemistry and ozone formation, the introduction has been revised as follows:

Lines 73-85: “In this study, an updated emission inventory with refined profiles of OVOCs and their VOC precursors is incorporated into the Community Multiscale Air

Quality (CMAQ) model to improve OVOC simulations over the Yangtze River Delta (YRD) region in China. Our previous work demonstrated the critical role of OVOC oxidation in enhancing atmospheric oxidation capacity and promoting ozone formation in this region, based on top-down emission adjustments constrained by field observations (Li et al., 2022a). To build upon those findings, we employ a speciation-improved bottom-up approach by integrating updated sector-specific source profiles into the YRD emission inventory, thereby refining the speciation of primary OVOCs and quantifying the contributions of their precursors. Based on this refinement, the roles of primary and secondary OVOCs in radical production and ozone formation, as well as the significance of primary OVOCs and traditional VOC precursors on ozone mitigation during a pollution episode, are investigated. These findings help bridge the knowledge gap regarding the complex sources and atmospheric evolution of OVOCs, elucidating their crucial roles in influencing urban ozone chemistry.”

Comment: 2. *The updated 2019 YRD emission inventory incorporates extensive source-resolved OVOC profiles, which is a major strength of the study. However, the methodology would benefit from a more explicit discussion of the uncertainties associated with these refinements. For example, it is not entirely clear how the 160 localized measurements and literature-based profiles were weighted or harmonized across sectors, and whether any sensitivity tests were performed to evaluate the impact of these updates on simulated OVOC concentrations.*

Response: Thank you for the insightful suggestion. In the revised manuscript, we have clarified the methodology for developing the source profiles. Specifically, our approach follows the Technical Guidelines for Compiling Integrated Emission Inventories of Air Pollutants and Greenhouse Gases (Ministry of Ecology and Environment, 2024). After sampling and data collection, the profile of each source category was developed through a two-step process:

(1) Sub-category Averaging: To minimize the influence of individual sample variability, measurements were averaged to derive stable, representative profiles for each sub-category. For example, diesel vehicle emissions were classified according to China VI, China V, and China IV emission standards, respectively. For industrial processes, representative profiles were derived according to specific industrial stages, raw materials, products, and fuel types. Similarly, for biomass burning emissions, fuel-specific profiles were established.

(2) Weighted Integration: The final integrated source profiles were synthesized by weighting the sub-category profiles according to their respective total VOC emission contributions in the study region.

We have revised the manuscript to reflect these details in Lines 116-134 as follows:

“The VOC composition of emissions from diesel vehicles, industrial processes, and residential biomass burning was characterized based on 160 localized, source-resolved measurements conducted in China. Specifically, twenty in-use heavy-duty diesel vehicles from five major brands were tested, encompassing China VI (n=6), China V (n=10), and China IV (n=4) emission standards. For industrial emissions, a total of 84 samples were collected from priority sectors, including petrochemical industries, chemical raw material production, and other chemical production sectors such as plywood production, coking, pesticides production, ink production, and rubber production. For residential biomass burning, 23 samples of the combustion of four representative biomass fuels (wood, corncob, bean straw, and corn straw) and two common coal types (anthracite and briquette coal) were collected from the stack nozzles of household stoves. Details of the sampling protocols and analytical procedures can be found in a previous study (Gao et al., 2023). VOC profiles for other sources, such as gasoline vehicles, were based on published literature (Wang et al., 2022a; Huang et al., 2024). To develop representative source profiles, a two-step aggregation method was employed. First, sub-category average profiles were derived by averaging individual samples within each specific emission standard, industrial stage, and types of raw materials, products, and fuels. Second, the integrated source profiles were synthesized by weighting these sub-category profiles according to their corresponding total VOC emissions. This method aligns with the national technical guidelines for integrated air pollutant emission inventories (Ministry of Ecology and Environment, 2024).”

Comment: 3. *The description of observational data is generally clear, but the treatment of PTR-QiTOF measurements requires slightly more detail. In particular, clarification on how fragmentation of alcohols was handled, how specific OVOC species were isolated from total protonated ion signals, and whether cross-validation with GC-MS was performed would enhance methodological transparency.*

Response: Thank you for this valuable suggestion. For most target OVOCs (such as aldehydes, ketones, and acids) measured by PTR-QiTOF, the molecular formula for individual mass spectral peaks was first constrained by jointly applying the elemental composition tool implemented in the Tofware software package v3.2.3 (Tofwerk Inc.), the PTR-MS spectral library (Pagonis et al., 2019), and the PubChem database. Based on these plausible molecular formulae, tentative compound identifications were further inferred by integrating previously reported source-specific emission profiles from the literature.

For species quantification, sensitivities for species with authentic standards were determined through calibration using multi-gradient known concentrations of given VOCs. For identified species lacking standards, their theoretical sensitivities were

estimated based on the correlations with kinetic rate constants of VOCs (Sekimoto et al., 2017). This approach has been successfully employed to identify reactive organic gases emitted from residential combustion in the YRD (Gao et al., 2022; 2023).

In the current study, small alcohols such as methanol and ethanol were detected using an online gas chromatography system equipped with a mass spectrometer and a flame ionization detector (GC-MS/FID). The results for major aromatic hydrocarbons and carbonyl compounds measured by PTR-QiTOF and GC-MS/FID show good agreement, as illustrated in Fig. S5 of Gao et al (2022).

We have revised the manuscript with detailed information on the treatment of PTR-QiTOF measurements and comparison between PTR-QiTOF and GC-MS/FID as follows:

Lines 148-160: “High time-resolution measurements of 77 OVOCs, including 14 aldehydes and ketones, 23 organic acids and esters, 10 furan compounds, and 30 oxygenated aromatic compounds, were recorded at a 10s interval using a Proton Transfer Reaction-Quadrupole interface Time-of-Flight Mass Spectrometer (PTR-QiTOF) at the Shanghai Academy of Environmental Sciences (SAES). Species were identified by jointly applying the Tofware software package v3.2.3 (Tofwerk Inc.), the proton transfer reaction mass spectrometry (PTR-MS) spectral library (Pagonis et al., 2019), the PubChem database, and source-specific emission profiles reported in literature (Hatch et al., 2017; Koss et al., 2018; Stockwell et al., 2021; Tanzer-Gruener et al., 2022; Coggon et al., 2021). Sensitivities for species with authentic standards were determined through calibration using multi-gradient known concentrations of given VOCs. For identified species lacking standards, their theoretical sensitivities were estimated based on correlations with kinetic rate constants of VOCs (Sekimoto et al., 2017). The raw data were screened to remove outliers (values below background levels) and missing data, and then averaged to hourly means.”

Lines 161-165: “In addition, C₂–C₁₂ hydrocarbons, C₂–C₅ carbonyls, and C₁–C₄ alcohols were measured using an online gas chromatography system equipped with a mass spectrometer and a flame ionization detector (GC-MS/FID, TH-300, Wuhan Tianhong Instruments, China) at an hourly resolution. For major aromatic hydrocarbons and carbonyl compounds, good agreement between measurements by PTR-QiTOF and GC-MS/FID was observed (Gao et al., 2022).”

Comment: 4. *This manuscript repeatedly distinguishes among “primary HO₂,” “newly generated HO₂,” and HO₂ derived from OVOC_{pri}, OVOC_{sec}, and RO₂ pathways. However, the conceptual boundaries among these categories remain*

somewhat unclear, especially regarding whether RO₂-to-HO₂ conversions are counted as primary or secondary production. I recommend adding a concise schematic or a table summarizing the definitions and accounting logic to help readers interpret Figs. 3c–e more clearly.

Response: Thank you for this insightful comment. We agree with the reviewer that the production pathways of HO₂ radicals were not clearly defined in the original manuscript. Given the strong coupling and rapid interconversion among HO₂, RO₂, and OH radicals, we now focus exclusively on primary radical production, defined here as radicals generated directly as products of the photolysis of OVOCs, O₃, and HONO, as well as the ozonolysis of OVOCs and unsaturated VOCs. Contributions from radical interconversion and cycling are therefore excluded. Primary radicals initiate atmospheric radical chemistry and trigger radical chain reactions, ultimately leading to ozone accumulation. By focusing on the contribution of OVOCs to primary radical production, we provide a clearer and more robust assessment of their role in ozone formation. The results indicate that OVOCs make substantial contributions to both HO₂ and RO₂ production, accounting for more than 90% of primary HO₂ production and 50–90% of primary RO₂ production. Although secondary OVOCs exert a more pronounced influence on primary peroxy radical production at the regional scale, primary OVOCs can contribute up to 50% of primary peroxy radical production in areas with substantial OVOC emissions. Given that HO₂ radicals are a key driver of NO-to-NO₂ conversion in regions strongly influenced by anthropogenic emissions, OVOCs, particularly primary OVOCs, play an important role in urban ozone production. The manuscript has been revised to include a discussion of primary radical production from OVOCs in Section 3.2 (now Section 3.3). A definition of primary radicals has been added in the revised manuscript, as follows:

Lines 323-327: “To elucidate the mechanism of daytime HO₂ radical production, the contributions of OVOCs to the formation of primary HO₂, RO₂, and RO_x radicals (RO_x = HO₂ + OH + RO₂) are assessed. Primary radicals refer to those generated through the photolysis of OVOCs, nitrous acid (HONO), and O₃ and the ozonolysis of OVOCs and unsaturated VOCs, while contributions from radical interconversion and cycling are excluded.”

Comment: 5. *The description of ozone changes (ΔO_3) would benefit from clearer definition. It is currently unclear whether the reported values (e.g., 0.90 ppb for HCHO) refer to domain-averaged responses, grid-level maxima, Shanghai city averages, or daytime peak ozone. Explicitly defining the metric, averaging period, and spatial domain would greatly improve interpretability and comparability of the sensitivity results.*

Response: Thank you for pointing out this ambiguity. We have clarified this at the

beginning of Section 3.3 (now Section 3.4) in Lines 383-384:

“The daytime average ozone responses to the complete removal of various VOCs (ΔO_3) at SAES”.

References

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