Response to Reviewer #1

General comments:

Comment: *OVOCs play a central role in tropospheric radical chemistry by enhancing the atmospheric oxidizing capacity and promoting the formation of secondary pollutants. This manuscript investigates the role of primary OVOCs in ozone formation over the YRD region by implementing updated, source-resolved OVOC emission profiles into CMAQ and combining model evaluation with process-based and sensitivity analyses. The topic is timely and relevant to the ACP readership, given the growing attention to VOC/OVOC inventories, VCP-related emissions, and radical budgets in polluted regions. However, several issues need to be addressed before the manuscript can be considered for publication in ACP.*

Response: We thank the reviewer for the positive and constructive feedback on our study. The comments have been very helpful in improving the clarity and overall quality of the manuscript. In response to the reviewer's suggestions, we have: (1) clearly defined primary and secondary OVOCs and radical sources; (2) refocused the analysis on the role of OVOCs in primary radical production (HO_2, RO_2, and RO_x) to improve the mechanistic understanding of ozone formation; (3) quantitatively characterized the concentrations of key OVOCs and the associated model biases; (4) strengthened the evaluation of model performance in simulating organic acids and discussed the uncertainties related to their budgets and emission contributions; and (5) reorganized Section 3.1 to improve the overall structure of the manuscript. 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.

Specific comments

Comment: *1. Line 19, The original statement "The model well captured the diurnal and seasonal variations of most OVOCs". Please clarify whether the model captures the variations in OVOC emission fluxes or in OVOC concentrations. In addition, support the statement more quantitatively (e.g. by quoting ranges of R, NMB, NME for key OVOC classes) rather than relying mainly on qualitative descriptions.*

Response: Thank you for pointing out this ambiguity. In Lines 19-21, we have revised it to: "The model reproduced the diurnal and seasonal variations of most observed OVOC concentrations, particularly carbonyl compounds, with moderate correlation coefficients of 0.40−0.79."

Comment: *2. Throughout the paper, "primary OVOCs", "emitted OVOCs" and "directly emitted OVOCs" are used. For clarity and consistency (also with the paper title), I recommend adopting "primary OVOCs" as the main term and defining it*

explicitly in Sect. 2 (e.g. primary = directly emitted from anthropogenic/biogenic sources; secondary = produced via VOC oxidation). Please ensure that the terminology is used consistently in the text, figures, and captions.

Response: We fully agree with your suggestion. To ensure consistency throughout the text, we have revised terminology, such as "emitted OVOCs" and "directly emitted OVOCs", to "primary OVOCs". Additionally, we have added a clear definition of primary and secondary OVOCs in Section 2.1, in Lines 143-145:

"In this study, primary OVOCs are defined as those directly emitted from anthropogenic and biogenic sources, whereas secondary OVOCs refer to those formed via the photooxidation of VOC precursors."

Furthermore, we have reviewed and revised all figure and table captions to ensure terminology consistency.

Comment: *3. Section 3.1, This section currently mixes the description of observed OVOC concentration characteristics with the discussion of model simulation results, which makes the content rather long and somewhat fragmented. I suggest splitting it into two subsections, separating the presentation of observations from the evaluation of model performance.*

Response: Thank you for the valuable suggestion, which has helped improve the clarity and organization of the manuscript. In the original manuscript, observations and model results were discussed together by species to facilitate a focused interpretation of OVOC characteristics and the associated model biases. To enhance readability and better align with your recommendation, we have reorganized this part of the manuscript by separating model evaluation from the regional analysis. Specifically, the original section has been divided into two subsections: Section 3.1, "Model evaluation", which emphasizes the evaluation of model performance while describing key observational features at the monitoring site; and Section 3.2, "Regional characteristics of OVOCs", which presents the simulated OVOC distributions and source contributions across the YRD region during the two episodes (EP1 and EP2). The section numbering in the remainder of the manuscript has been updated accordingly.

Comment: *4. Section 3.1, For some species (e.g. acids, alcohol) the discussion emphasizes underestimation or overestimation, but quantitative information on observed mean/median concentrations is limited. It would be helpful to briefly summarize typical concentration ranges for the main OVOC classes in the main text or in a supplementary table, to give readers a clearer sense of magnitude.*

Response: Thank you for the valuable suggestion. The mean observed and predicted OVOC concentrations at the monitoring site have been included in the original Table S5. To ensure the representativeness of the results, CIIE-period (temporary emission

control measures during the China International Import Expo 2019) data were excluded, thereby avoiding model discrepancies caused by temporary emission regulations and accurately reflecting typical emission scenarios. We have also included descriptions of OVOC concentrations at the monitoring site in the revised text as follows:

Lines 183-185: "Among all the observed OVOCs, alcohols emerged as the dominant species in spring (EP1), with ethanol exhibiting the highest median concentrations (6−12 ppb), which declined to 1.9−4.6 ppb in fall (EP2)."

Lines 196-197: "Formic acid and acetic acid were the most abundant organic acids during both episodes, with the average concentrations of 0.15 (1.95) ppb and 1.88 (2.59) ppb in the EP1 (EP2) period, respectively."

Lines 227-229: "HCHO and acetone (ACET) were the most abundant aldehyde and ketone species, with average observed concentrations of 2.52 (2.58) ppb and 5.75 (1.89) ppb during EP1 (EP2), respectively."

Lines 249-251: "HCHO, MEOH, ACET, and acetaldehyde (CCHO) were the dominant species (Fig. S8), with concentration ranges of 2−8 ppb, 2−4 ppb, 2−4 ppb, and 1−3 ppb, respectively."

Lines 254-256: "The concentrations of ETOH, HCOOH, and CCOOH fell in ranges of 1.0–3.0 ppb, 0.1–0.4 ppb, and 0.5–2.0 ppb, respectively. Given the substantial underestimations of all three species, their actual concentrations are likely higher than the model predictions."

Comment: *5. Lines 213-215: Is there any evidence or supporting analysis to substantiate the conclusion that the biogenic contribution is higher during the warm season?*

Response: We have included a regional distribution of the average MEOH emission rates and contributions from biogenic sources across the YRD region in EP1 and EP2 in the supplement Fig. S9 (as shown below). The emission rates of MEOH are much higher during EP1 than during EP2. The main text has been revised accordingly as follows:

Lines 251-253: "High levels of HCHO, ACET, and CCHO mainly occurred in areas strongly influenced by anthropogenic emissions, where MEOH was predominantly concentrated in regions affected by biogenic emissions in the southern and southwestern YRD (Fig. S9)."

Lines 258-260: "The higher simulated MEOH concentrations in EP1 relative to EP2 may be partially attributed to stronger contributions from biogenic sources during the warm season (Fig. S9d, h)."

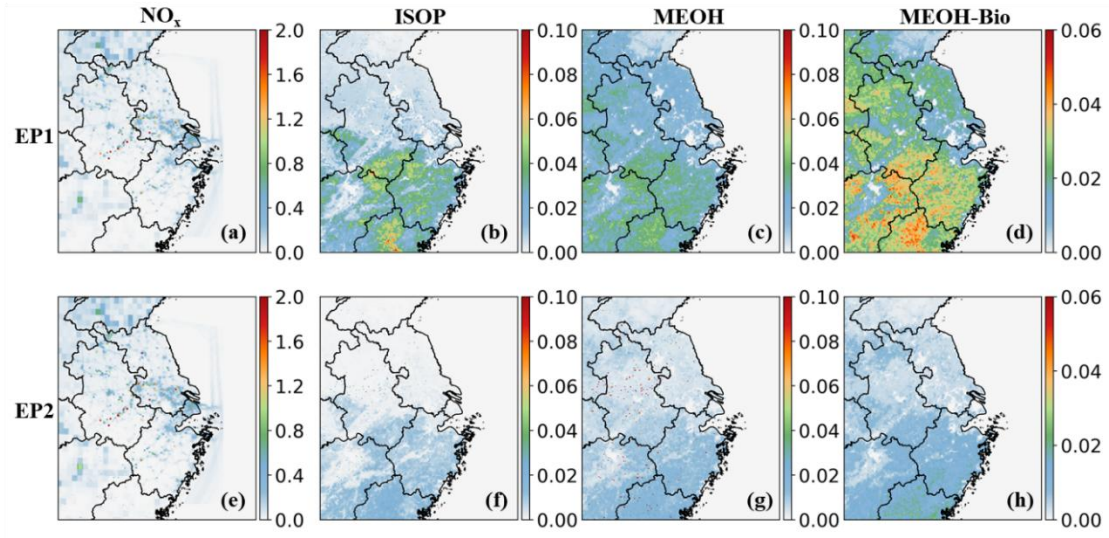

Figure S9. Average emission rates of NO_x, isoprene, MEOH, and biogenic MEOH during EP1 and EP2. Units are mole s^{-1}.

Comment: *6. Section 3.2, The authors acknowledge missing or simplified pathways for the production and loss of small aldehydes and organic acids. Given the importance of these processes for formic and acetic acid biases, please expand slightly on which multiphase/heterogeneous reactions are included (e.g. glyoxal/methylglyoxal uptake, aqueous-phase oxidation) and which are missing, and discuss how these omissions could affect both OVOC budgets and the derived role of primary emissions.*

Response: Thank you for the insightful comment. In the current model, heterogeneous losses of glyoxal and methylglyoxal are parameterized by first-order reactions, with the rates determined by uptake coefficients (γ). We adopt the values of γ reported by Everns and Volkamer (2010), 0.016 during daytime and a constant loss rate of 3.33×10^{-4} s^{-1} at night, which have been applied in our previous work and described in the original manuscript in lines 87-89:

"Several model updates, including heterogeneous reactions of sulfur dioxide (SO_2), NO_2, glyoxal, and methylglyoxal, were implemented as described in a previous study (Mao et al., 2022)."

However, the uptake of these dicarbonyl species is affected by their interactions with inorganic aerosols, known as "salting effects", which is not considered in the current model. Once uptake into the aqueous phase of aerosols, both dicarbonyls can be oxidized to produce formic and acetic acids (and other products) through complex reactions. These processes are poorly represented in most commonly used chemical transport models, including CMAQ, with all the products lumped into a surrogate species. The simplified treatment of the heterogeneous chemistry of these dicarbonyl species could partially explain the underestimation of methylglyoxal, formic acid, and acetic acid. We have clarified this in the revised manuscript in Lines 208-219:

"Therefore, the underestimation of both formic and acetic acids may partially stem from insufficient representation of secondary production. Observations showed that formic acid exhibited moderate to strong correlations with its precursor methylglyoxal in both periods. Laboratory studies have demonstrated that both formic and acetic acids can be produced via aqueous-phase reactions of glyoxal and methylglyoxal (Yu et al., 2011; Zhang et al., 2021; Sui et al., 2017; Lim et al., 2013), with uptake modulated by interactions with inorganic aerosols (i.e., salting effects) (Waxman et al., 2015; Kampf et al., 2013). In the current model, these heterogeneous processes are represented by first-order reactions, with rate constants determined by fixed uptake coefficients (γ=0.016 during daytime and a constant loss rate of 3.33×10^{-4} s^{-1} at night), and all products are lumped into a single surrogate species. The simplified treatment of heterogeneous chemistry likely leads to an underestimation of formic and acetic acids, particularly under high aerosol loadings in urban environments, where salting-out effects reduce their solubility in the aqueous phase (Babaei-Gharehbagh et al., 2025)."

Other secondary production of formic and acetic acids, such as multiphase reactions of HCHO (to produce formic acid), photochemical aging of aerosols, are not included in the current model. In addition, the yield of formic and acetic acids from precursor VOCs may be underestimated and contribute to the model biases of these organic acids. This has been clarified in the revised manuscript in Lines 219-223:
"Other sources of model bias may include missing secondary formation pathways, such as multiphase reactions of HCHO and photochemical aging of aerosols, and underestimated yields of formic and acetic acids from precursor VOCs (Yuan et al., 2015; Millet et al., 2015; Permar et al., 2023; Jiang et al., 2023; Cope et al., 2021; Franco et al., 2021; Malecha and Nizkorodov, 2016; Shen et al., 2026)."

Inadequate representation of secondary production may lead to an overestimation of emission contributions to formic and acetic acids. However, the discrepancies between the model and observations may also partially arise from underestimated emissions of these two species. As a result, the combined effects of these factors make it difficult to quantitatively assess the contributions of emissions to their concentrations. We have added discussions in the revised manuscript to address the potential impacts on their budgets and the associated emission contributions, as detailed below:
Lines 274-276: "Notably, the emission contributions of CCOOH may be biased due to uncertainties in emission inventories and chemical production in the model."

Comment: *7. Section 3.2, The terminology for HO2 sources (primary from VOC/OVOC oxidation, "newly generated" from photolysis and O_3 reactions, etc.) is central to the conclusions. I recommend adding a concise schematic or a table defining each category before Fig. 3 and clarifying whether "primary" HO2 excludes contributions from RO2 to HO2 recycling. This will help readers interpret Fig. 3c-e and the subsequent regional analysis.*

Response: Thank you for this constructive comment. Because HO_2, RO_2, and OH radicals are closely coupled and undergo rapid interconversion, the revised manuscript focuses on the production of primary (newly generated) radicals formed directly via photolysis (OVOCs, HONO, and O_3) and ozonolysis (OVOCs and unsaturated VOCs) reactions, in which radicals are generated solely as reaction products. Contributions from radical interconversion and cycling are therefore not included. 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 manuscript has been revised accordingly to include a discussion of primary radical production from OVOCs in Section 3.3. Accordingly, a definition of primary radicals has been added to the revised manuscript, as described below:

Lines 323-327: "To elucidate the mechanism of daytime HO_2 radical production, the contributions of OVOCs to the formation of primary HO_2, RO_2, and RO_x radicals (RO_x = HO_2 + OH + RO_2) are assessed. Primary radicals refer to those generated through the photolysis of OVOCs, nitrous acid (HONO), and O_3 and the ozonolysis of OVOCs and unsaturated VOCs, while contributions from radical interconversion and cycling are excluded."

Technical comments

Comment: *1. Lines 41-43, please insert relevant reference for the box models results.*

Response: References on box model studies have been added in Line 45.

Comment: *2. Line 149, I suggest adding the word "concentration" to the section title to more clearly reflect the main focus of this subsection.*

Response: Thank you for the comment. To improve the clarity and overall organization of the manuscript, as suggested by the reviewer, the original section has been divided into two separate sections: "Model evaluation" and "Regional characteristics of OVOCs".