A letter of Response to Reviewers

Title: Characteristics and sources of NMVOCs and the O_3-NO_x-NMVOCs relationships in Zhengzhou, China

We thank the reviewer for reading our manuscript and providing valuable comments and suggestions. We have carefully considered all comments and revised the manuscript accordingly. We believe that we have adequately addressed your comments. To facilitate your review, the comments are in black, and our responses are in blue. Major changes made in response to these comments are highlighted in yellow in the revised manuscript, while our minor changes are marked in red font. Please note that the line numbers referred to below correspond to the corrected version.

Referee comments

10 "…important precursors of ozone (O_3) generation" add "under conditions of sufficient nitrogen oxides"

Response: Thank you for your valuable feedback.

We have made the suggested modification to our manuscript. The original sentence on line 10, "Nonmethane volatile organic compounds (NMVOCs) are important precursors for the formation of ozone (O_3)," has been revised to: "Nonmethane volatile organic compounds (NMVOCs) are important precursors of ozone (O_3) formation under conditions of sufficient nitrogen oxides." (Line 10-11)

19-20 The sentence "An observation-based mode was applied …" is unclear. I suggest "We explore observations of the O_3-precursors

relationship and propose observation-oriented O_3 control strategies."

Response: Thank you for your valuable feedback.

We have revised the sentence "An observation-based modeling approach was employed to investigate the O_3-precursors relationship." to "We explore observations of the O_3-precursors relationship and propose observation-oriented O_3 control strategies." to improve clarity. (Line 19-20)

22 Change "in anthropogenic" to "in the anthropogenic"

Response: Sorry for the mistake.

We have made the correction by changing "in anthropogenic" to "in the anthropogenic". (Line 21)

44 "NMVOCs concentration varies" should be "NMVOC concentrations vary" (change every occurrence).

Response: Sorry for the mistake.

We have made the correction by changing "NMVOCs concentration varies" to "NMVOC concentrations vary" for every occurrence in the manuscript. (Line 43)

90 The more usual symbol for percentile is "%ile", so "8H-90%ile".

Response: Thanks for the suggestion.

We have made the correction by changing "(O_3-8H-90per)" to "(O_3-8H-90%)." (Line 88-89)

114-117 "1 meter" is incredibly close. Please say something more specific?

Response: Thank you for your valuable feedback.

Regarding the mention of "Within a radius of 1 meter" in manuscript, it was indeed an error on my part. I intended to refer to a radius of 1 kilometer, not 1 meter. We have conducted field investigations, and we have corrected this mistake. (Line 114-115)

166 Section 2.5 is still rather obscure. Please provide the general differential equation being solved by the model (e.g., dX/dt = P – L(X), where X is the chemical species, P is all the production terms and L(X) all the loss terms). Since the model is described as being independent of emissions and (incorrectly – see line 190) meteorological parameters, I imagine it is being used to calculate a steady-state solution appropriate for every hour (cf.). Is this correct?

MCM. Was it used to calculate other factors in your model?

Response: Thanks for the comments. We apologize for any obscurity.

1. The OBM used in this study iteratively solves a set of ordinary

differential equations (ODEs) that describe the evolution of species concentrations over time. For species with observation concentrations (normally constituted by primary NMVOCs and NO_x), the horizontal convection and emission are normally significant. In a zero-dimensional model, those processes are lumped into R_{other} term. Within each iteration, R_{other} is determined by the Eq (6):

$$R_{other} = \left(\frac{\partial C_i}{\partial t}\right)_{obs} - \left[P_i - L_i C_i - \frac{1}{H} v_d C_i - \frac{1}{H}\frac{dH}{dt}\left(C_i - C_{i,bg}\right) + R_{aero,i} + R_{aq,i}\right] \quad (6)$$

Where P_i and $L_i C_i$ represents total the represents all the production and loss rate, respectively; $\frac{1}{H} v_d C_i$ represents the sum of mixing and deposition rates; $\frac{1}{H}\frac{dH}{dt}\left(C_i - C_{i,bg}\right)$ accounts for the mass exchange rate with background atmosphere; $R_{aero,i}$ and $R_{aq,i}$ are the rate of aerosol and aqueous processes, respectively; $\left(\frac{\partial C_i}{\partial t}\right)_{obs}$ is the real rate of change in concentration which is interpolated from hourly observed data points.

With the value of R_{other} term explicitly determined from Eq (6), the concentrations of all species are then predicted by integrating the governing equation (7):

$$\frac{\partial C_i}{\partial t} = P_i - L_i C_i - \frac{1}{H} v_d C_i - \frac{1}{H}\frac{dH}{dt}\left(C_i - C_{i,bg}\right) + R_{aero,i} + R_{aq,i} + R_{other} \quad (7)$$

New iterations start with updated R_{other} values based on the concentrations predicted from the previous step, until converged solution is obtained.

Additionally, we have included the above content in the manuscript. (Line 172-186)

2. Although the input data for our study has a resolution of one hour, the actual time step for solving the model is less than 100 seconds, such small time-step guarantees the accuracy/reliability of the model solution (i.e. the results are independent from the integration time-step size). The model performs interpolation on the observed values. The statement in the manuscript has been changed to: “Briefly, OBM is a zero-dimensional model that assumes a well-mixed atmosphere, and combined with atmospheric chemical mechanisms, simulates the O_3 production rate and the corresponding O_3 concentration at a given time.” (Line 168-171)

3. The Master Chemical Mechanism (MCM) is a near-explicit chemical mechanism used to describe gas-phase chemistry. Its latest version, MCMv3.3.1, includes over 5800 species and 17,000 reactions. The MCM was not used to calculate other factors in our model. Instead, it served as a reference mechanism

for the chemical reactions included in our model.

168 Change “employed to estimate the effect of changes of what in O_3 precursors” to something like “employed to estimate the effect of changes in precursors on O_3”.

Response: Thanks for the suggestion.

We have revised the sentence “OBM based on the Master Chemical Mechanism (MCM v3.3.1; https://mcm.york.ac.uk/MCM/) was employed to estimate the effect of changes of what in O_3 precursors.” to “OBM based on the Master Chemical Mechanism (MCM v3.3.1; https://mcm.york.ac.uk/MCM/) was employed to estimate the effect of changes in precursors on O_3.” to improve clarity. (Line 166-167)

169-170 Change “a good mix” to “a well-mixed atmosphere”, if this is what is meant.

Response: Thanks for the suggestion.

We have made the correction by changing “a good mix” to "a well-mixed atmosphere.” (Line 169)

190-191 You mean that the concentration of NO was held constant? This seems like a very questionable assumption and would be equivalent to adding a source of NO_3 to the model.

Response: Thank you for your valuable feedback.

In the model, concentration of NO is not held constant, as it is calculated by solving the Eq (6-7). The solution procedure is described in the response to above comment. Regarding your comment about the concentration of NO being held constant.

194 The model will use time steps much smaller than 1 hour. Do you mean the model is stepped forward for 1 hour of simulation?

Response: Thank you for your insightful comments.

We apologize for the inaccuracies in our manuscript, which have been removed. Regarding the time steps, we would like to clarify that the model's time steps are less than 100 seconds, not 1 hour. However, the output time step of the model is indeed 1 hour. We have addressed the specific calculations and settings of the OBM in our previous responses.

203 Do you mean that the O_3 is initialised to zero? That seems unlikely. I think you have an initial value which is allowed to evolve for the duration of the model run. Since O_3 evolves relatively slowly, it may be quite possible to have a good IOA without the model working well.

Response: We apologize for the confusion caused by our inappropriate description.

Regarding your query about the initialization of O_3, we would like to clarify that the initial concentration of O_3 in our model is not zero. Instead, we set the initial O_3 concentration to 0.04 ppmv, which represents the background ozone concentration in clean air. Additionally, the meaning in the manuscript is that we do not input the observed O_3 concentration into the OBM, but rather simulate the O_3 concentration using the OBM.

206 Without a better description of the model set up, you cannot claim that it is reliable.

Response: Thanks for the suggestion.

We have provided a detailed description of the OBM's simulation methodology in our response above. Additionally, we have added a table in the supplementary materials that outlines the specific settings of the model (Table S2). We believe these additions enhance the understanding of the model setup and its reliability.

262 "average" or "mean", not both.

Response: Sorry for this mistake.

We have revised the sentence as follows: "During the entire period, the concentration of TNMVOCs varied from 10.0 to 60.0 ppbv, with an average concentration of 23.0 ± 8.0 ppbv." (Line 275)

303-306 The diurnal pattern in ozone must be a combination of mixing (especially as the nocturnal boundary layer breaks up) and chemistry, so it is not correct to ascribe high ozone mixing ratios to in-situ production alone. These sentences should be modified.

Response: Thank you for your comments.

We have referenced relevant literature. Based on this, we have revised the relevant section. The updated text now reads:

"This diurnal pattern is influenced by strong photochemical reactivity, boundary layer processes, and meteorological parameters. Higher O_3 production during the day indicates significant contributions from both photochemical reactions and atmospheric mixing processes." (Line 318-321)

316 The reference for this sentence is not appropriate. Please cite one or more of the foundational papers on isoprene production from plants from the 1980s.

Response: Thank you for your feedback.

We apologize for the oversight regarding the reference for the sentence on isoprene production from plants. We have revised the manuscript to include the following references:

1. Guenther, A. B., Zimmerman, P. R., Harley, P. C., Monson, R.

K., and Fall, R.: Isoprene and monoterpene emission rate variability: Model evaluations and sensitivity analyses, J. Geophys. Res-Atmos., 98, 12609-12617, https://doi.org/https://doi.org/10.1029/93JD00527, 1993.

2. Sharkey, T. D., Singsaas, E. L., Vanderveer, P. J., and Geron, C.: Field measurements of isoprene emission from trees in response to temperature and light, Tree. Physiol., 16, 649-654, https://doi.org/10.1093/treephys/16.7.649, 1996.

We hope these references meet the standards you suggested. (Line 335-336)

320-321 Couldn't the bimodal shape also come from reaction with OH, since OH peaks in the middle of the day? Your model should be able to calculate this.

Response: Thank you for your valuable feedback.

To address your comment, we have now included an analysis of the OH radical concentrations simulated by our model. The daily variation of OH radical indeed shows a peak around noon, which could contribute to the observed decrease in isoprene concentrations. We have included a plot of the daily variation of OH radical in the revised manuscript (Fig. S5) and updated the text to reflect this additional consideration.

Additionally, we have added the following sentence to further explain the influence of OH radical on the bimodal shape of isoprene concentration: "Additionally, the concentration of OH radicals peaks at noon (Fig. S5), leading to the rapid oxidation of isoprene by OH radicals, which further contributes to the observed bimodal pattern (Paulot et al., 2009)." (Line 337-339)

We believe these additions enhance the understanding of the factors influencing the bimodal shape of isoprene concentration. Thank you again for your constructive comments.

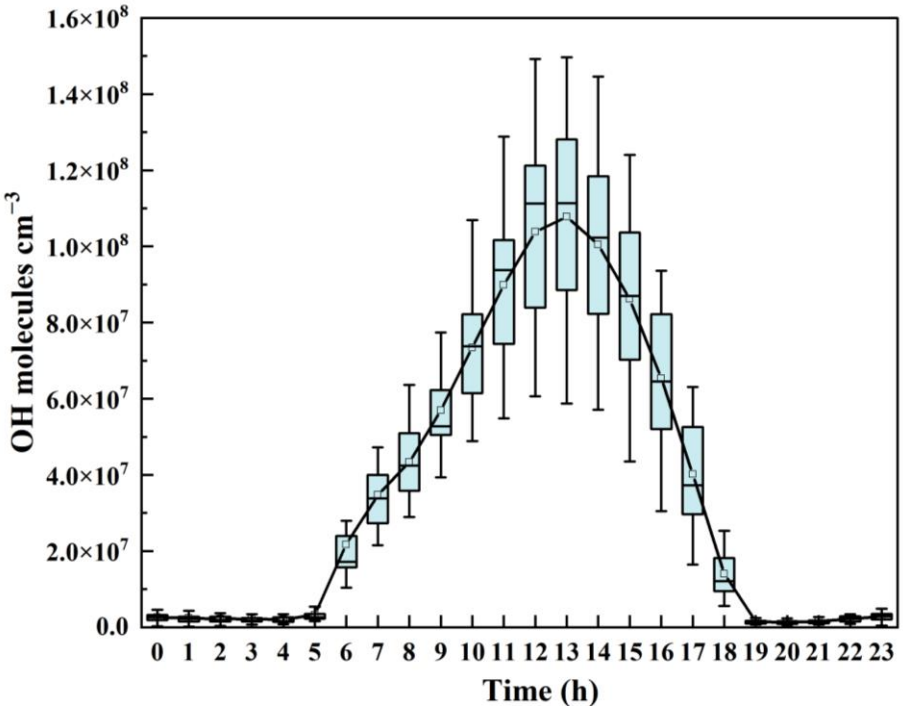

Fig. S5. Model-simulated daytime average diurnal variations in OH concentrations.

References

Paulot, F., Crounse, J. D., Kjaergaard, H. G., Kürten, A., St Clair, J. M., Seinfeld, J. H., and Wennberg, P. O.: Unexpected Epoxide Formation in the Gas-Phase Photooxidation of Isoprene, Science, 325, 730-733, https://doi.org/10.1126/science.1172910, 2009.

346-350 These sentences are not consistent. You argue that E/X gives information about photochemical age, not source differences. Fig 4. “ratio” not “ration”

Response: Thank you for your feedback. We appreciate your attention to detail.

We have revised the first sentence of the manuscript as you suggested. It now reads: “Since m/p-xylene and ethylbenzene share a common source but differ in their OH radical reaction rate constants, the E/X ratio can be used to understand source characteristics.” (Line 363-364)

Additionally, we have corrected the typographical error in Figure 4, changing “ration” to “ratio”.

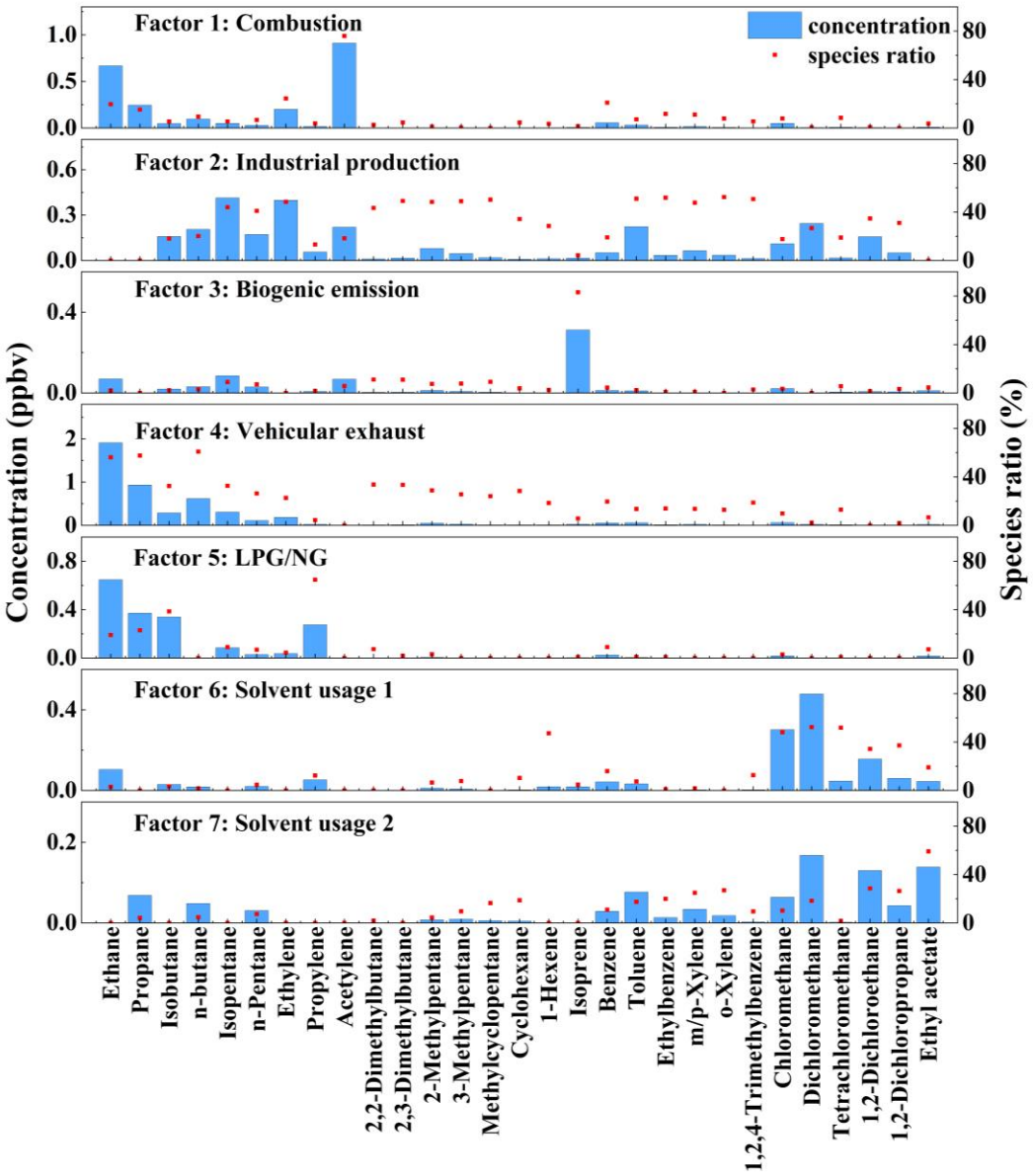

Figure 4. Source profiles and contributions of NMVOCs during the observation period.

444-445 Please correct: "Among AVOCs, aromatics had the highest RIR value, followed by alkanes and aromatics."

Response: Thank you for pointing out the error in the sentence. I have corrected it as follows:

The original sentence: "Among AVOCs, aromatics had the highest

RIR value, followed by alkanes and aromatics." has been corrected to: "Among AVOCs, aromatics had the highest RIR value, followed by alkenes and alkanes." (Line 461-462)

536 Change "The summer O_3 pollution has always been an important environmental issue in Zhengzhou" to something like "Summer O_3 pollution remains an important environmental issue in Zhengzhou."

Response: Thank you very much for your valuable feedback. I have revised the sentence as per your suggestion. The original sentence: "The summer O_3 pollution has always been an important environmental issue in Zhengzhou" has been changed to: "Summer O_3 pollution remains an important environmental issue in Zhengzhou." (Line 554)