Responses to Reviewer #1

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Title: Response relationship between atmospheric O_3 and its precursors in Beijing based on smog chamber simulation and a revised MCM model

We sincerely appreciate the your careful review and valuable guidance. The manuscript has been thoroughly revised according to the your suggestions, and all changes have been clearly highlighted using the Track Changes mode in the revised version. Enclosed please find our point-by-point responses to your comments for your kind consideration.

Responses to your comments

This manuscript presents a well-structured and scientifically rigorous study that combines smog chamber experiments with a revised MCM box model to improve the simulation of O_3 formation and its sensitivity to precursors. The work is highly relevant to current air quality challenges, particularly in regions like Beijing suffering from severe O_3 pollution. The methodological approach is sound, the results are clearly presented, and the conclusions are well-supported by the data. The inclusion of chamber wall effects and unidentified NO_2 sinks represents a valuable contribution to the field. I recommend acceptance after minor revisions.

Response: Thank you very much for your positive comments.

General comments

1. The authors note that the NO_2 sink rate constant used is higher than values reported in previous studies (Page 12, Line 285). A brief justification or speculation on why this might be the case (e.g., unaccounted surfaces, synergistic effects) would strengthen the discussion.

Response: The high NO_2 sink rate constant is likely attributable to physical dilution processes, which were not accounted for in the previous study. Previously, we attempted to simultaneously use NO and NO_2 as constraints. Under that configuration, the impact of varying physical dilution rates on O_3 simulation results was indeed minimal (as illustrated in the Figure R1), which led us to overlook the significance of the physical dilution process in the earlier stages of our study. However, as discussed in the revised manuscript, to more accurately evaluate the influence of ground-related reactions on O_3 formation, we transitioned to a more scientific setup where only NO is constrained. Under this revised configuration, the physical dilution rate exhibits a significant impact on the O_3 simulation results, as detailed in the Figure R2 of the revised manuscript. We have realized that neglecting physical processes in ambient atmospheric simulations is inappropriate, as it was the primary cause for the previous discrepancies where simulated NO_2 and O_3 concentrations deviated significantly from observations. However, the challenges in accurately characterizing atmospheric physical processes prevent further investigation into O_3 simulation performance and O_3 sensitivity (EKMA). Consequently, the focus of this study was shifted toward a systematic evaluation of the impact of ground-related reactions on the formation of O_3 and HONO. We conclude that ground-mediated reactions exert a significant influence on HONO, whereas their impact on O_3 is negligible. Detailed modifications have been implemented after line 296.

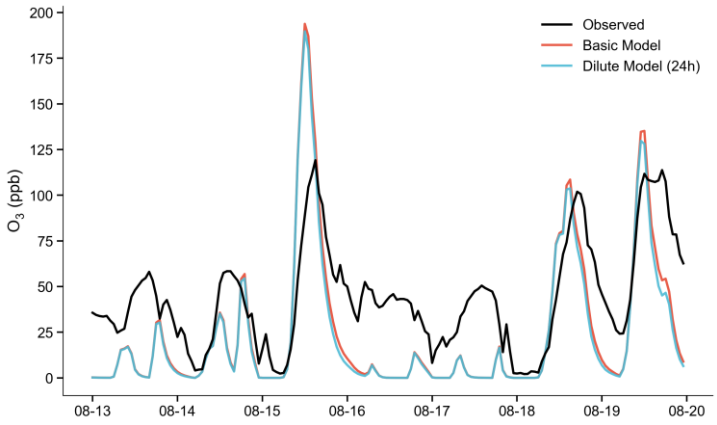

Figure R1. Comparison of observed and simulated O_3 concentrations across different model scenarios. The

basic model results are obtained with NO and NO_2 concentrations constrained. The dilute model results reflect the impact of a 24 h physical dilution process on the simulated O_3 levels.

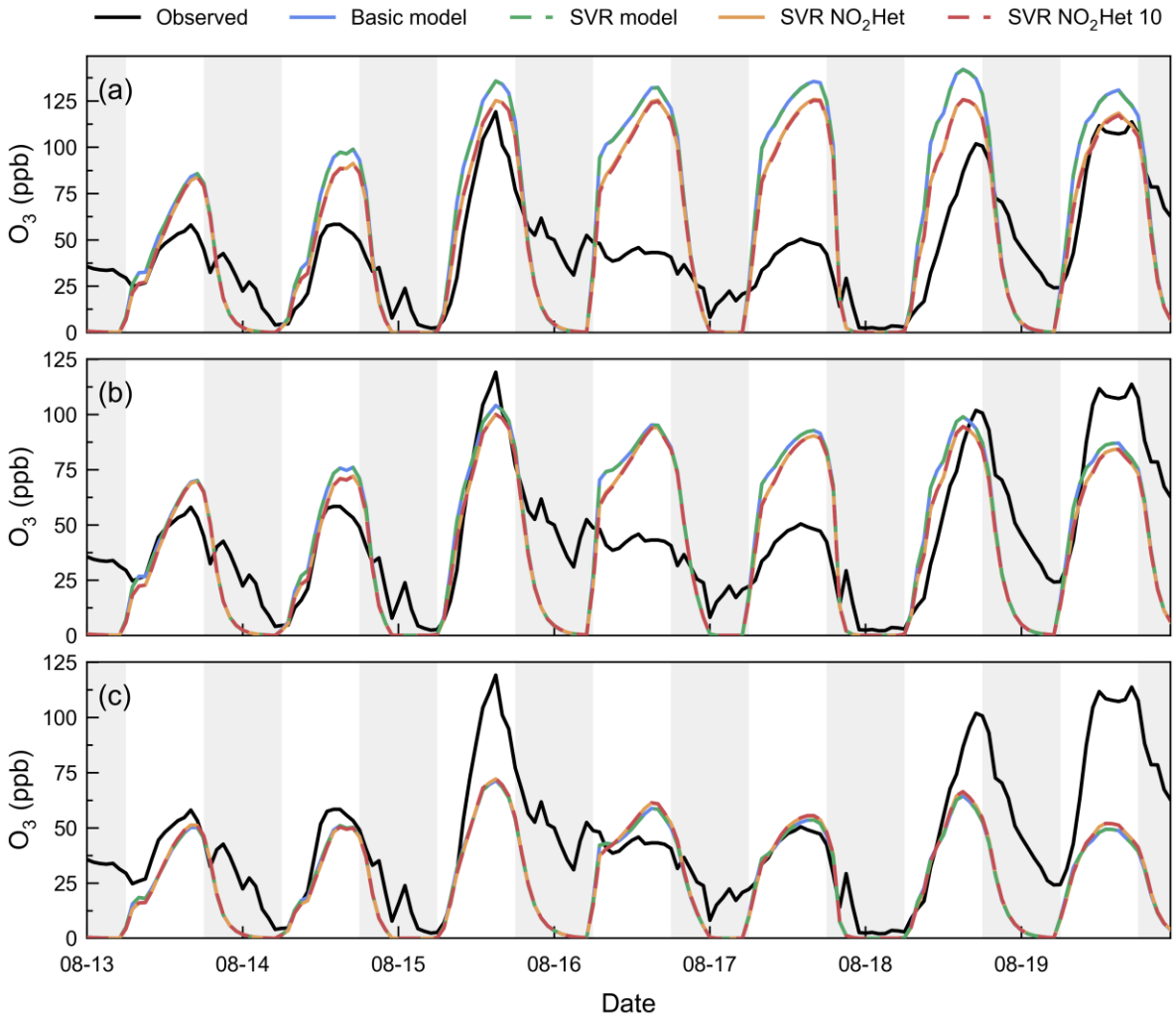

Figure R2. Comparison of observed and simulated O_3 concentrations under physical dilution rates of (a) 5.80×10^{-6} s^{-1}, (b) 1.16×10^{-5} s^{-1} and (c) 2.32×10^{-5} s^{-1}. The black curves represent the observed O_3 concentrations, and the shaded areas denote nighttime periods. Compared to the basic model, the SVR model incorporates ground-related reaction mechanisms derived from chamber experiments. The SVR NO_2Het model further adjusts the ground-related NO_2 heterogeneous reactions based on the SVR model. In the SVR NO_2Het 10 model, the rates of all reactions, excluding the NO_2 heterogeneous reactions, are scaled up by a factor of 10 relative to the SVR NO_2Het model.

2. The authors should briefly discuss the potential uncertainties in the uptake coefficients (γ) used for aerosols. Could the use of a constant γ, which may vary with aerosol composition and phase state, partly explain the need for such a large additional sink? A sentence or two on these limitations would be helpful.

Response: The nocturnal aerosol uptake coefficient varies within the range of 2×10^{-7} to 1×10^{-5}, and we adopted a relatively high constant value of 8×10^{-6} (Liu et al., 2019). Similarly, a high uptake coefficient was applied for daytime conditions, with a peak value of 1×10^{-3} (Wong et al., 2013). However, despite moderate improvements in O_3 simulation performance, a substantial discrepancy between modeled and observed values persists. This prompted us to explore alternative explanations, leading to the conclusion that the significant model-measurement gap is primarily driven by the neglect of physical processes.

3. The discussion of the sensitivity shift (Section 3.6) could be enhanced by more explicitly linking the increased radical concentrations to the enhanced VOC sensitivity. A concise explanation could be: "The introduction of the NO_2 sink reduces NO_2 levels, which in turn lowers NO concentrations due to photo-stationary state relationships. Lower NO levels diminish the titration of O_3 and, more importantly, reduce the scavenging of HO_2 and RO_2 radicals by NO. This increases the radical chain length and amplifies the role of VOC oxidation in O_3 production, thereby shifting the system towards greater VOC sensitivity."

Response: We are very grateful for your insightful suggestion, which has significantly enhanced our understanding of O_3 formation chemistry. We originally intended to simulate radical concentrations using our model to validate the theory you proposed. We acknowledge that the exact magnitudes of NO_2 sinks and physical processes are difficult to determine with the available data. Therefore, we have opted to omit a comprehensive discussion on the sensitivity transition to avoid over-interpretation.

4. In the conclusion or discussion, it would be valuable to explicitly state that while the box model is excellent for isolating chemical mechanisms, the identified NO_2 sink rate constant is an "effective" rate that may also compensate for the lack of physical processes like advection and vertical dilution. A recommendation for future work using a 3D model with these revised chemical mechanisms to validate and spatially contextualize the findings would be a logical and strong ending point.

Response: We fully agree that the NO_2 sink identified in our previous model effectively functioned as a surrogate to compensate for physical processes such as advection and vertical dilution. However, whether this compensatory effect introduces additional uncertainties warrants further investigation. Our findings highlight that physical processes exert a substantial influence on O_3 simulations. The robust capability of 3D models to resolve these physical dynamics facilitates a more rigorous investigation into the chemical mechanisms driving O_3 formation.

Revised text as it appears in line 359-360 of the text:

This underscores the necessity of employing three-dimensional models to further explore the complexities of O_3 chemistry.

Technical comments

1. "the complex of atmospheric conditions" (Page 2, Line 39) might be better expressed as "the complexity of atmospheric conditions".

Response: It has been revised.

Revised text as it appears in line 38-40 of the text:

However, the complexity of atmospheric chemical processes poses challenges for accurate characterization, resulting in significant biases in sensitivity analysis of O_3 formation (Li et al., 2018; Xue et

al., 2021; Qu et al., 2021; Chen et al., 2024), and triggering debates over optimal precursor control strategies.

2. Page 3, Table 1, NO_x concentration values are lower than those of NO, resulting in a negative NO_2 Correction should be applied to NO_x concentrations (including both NO and NO_2). Additionally, the symbol "–" can be used to indicate that a reactant was not added to the chamber.

Response: The instances in Table 1 where NO_x appeared lower than NO was due to measurement uncertainties of the instruments. Since NO_2 was not intentionally added to the smog chamber in these cases, any measured NO_2 values that fell below zero were set to 0, and the initial NO_x values were adjusted accordingly. Furthermore, we have changed the symbol used to denote components that were not added from "0" to "–" to ensure better clarity.

3. Page 6, Line 151: change "revised model in experiment Iso&Tol02 were" to "revised model in experiment Iso&Tol02 are" for grammatical agreement.

Response: It has been revised.

Revised text as it appears in line 174-175 of the text:

The NMB values for O_3 simulated by the basic model, revised model in experiment Iso&Tol02 are -83.9 % and -19.0 %, respectively.

4. Page 7, Table 2: "Refered" should be "Referred".

Response: It has been revised.

5. "the slope of the ridge line of the EKMA curves" (Page 9, Line 203) is correct, but consider using

"ridgeline" as one word for consistency.

Response: It has been revised.

Revised text as it appears in line 235-236 of the text:

Meanwhile, it can be found that, whether in the toluene only system or in the toluene isoprene mixed system, the slope of the ridgeline of the EKMA curves derived from the revised model changes.

6. "the uptake coefficient in the chamber wall is equal to that in the atmospheric ground" (Page 9, Lines 218-219) – consider rephrasing to "on the chamber wall" and "on the ground surface" for precision.

Response: It has been revised.

Revised text as it appears in line 254-257 of the text:

Given the complexity of surface types in the ambient environment and the significant variability in uptake coefficients across different surfaces (Vandenboer et al., 2013; Liu et al., 2019; Trick, 2004), we initially assumed that the uptake coefficient on the chamber wall is equivalent to that on the ground.

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