Response to Reviewer 2

Comments:

This paper focuses on the long-term changes in ozone concentration in the Pearl River Delta (PRD) region during 2001–2020, as well as the contribution of climate-driven biogenic volatile organic compounds (BVOCs) to ozone formation. By using the WRF-CMAQ model and the MEGAN model, in combination with machine learning analysis, the study reveals the key influence of BVOCs on ozone formation potential. Climate-driven BVOC emissions enhance the atmospheric oxidation capacity and accelerate ozone formation, thereby weakening or even offsetting the effects of anthropogenic emission reductions. These emissions contribute 6.2 ppb to ozone production, leading to an unexpected rise in ozone levels. This research deepens the understanding the complex interactions between natural source emissions and anthropogenic control strategies, and it provides practical reference value for the formulation of regional air pollution control policies. However, some clarifications and changes are necessary.

Response to Reviewer 2: We sincerely appreciate your time and effort in reviewing this manuscript. Your insightful comments and suggestions have greatly helped us improve the quality of our work. We have carefully revised the manuscript with revisions made in red color. We believe this revised version is better organized, and our point-by-point responses and revisions are detailed below.

Point-to-point response

1. **The study utilizes a random forest (RF) model to analyze the primary driving factors of BVOC emissions and employs SHAP values to explain the contributions of various meteorological factors. However, the validation process of the RF model is insufficiently detailed, with no mention of cross-validation methods. It is recommended that the authors supplement the model validation.**

Reply: Thanks for the suggestion. We have added a 10-fold cross-validation in this manuscript. Please see our revision "To ensure the robustness of the results, we performed a 10-fold cross-validation, achieving an R^2 (coefficient of determination) of 0.78 and an MAE (mean absolute error) of 0.73 (Fig S1). These metrics indicate that the machine learning model effectively reproduces BVOC emissions.” in the manuscript.

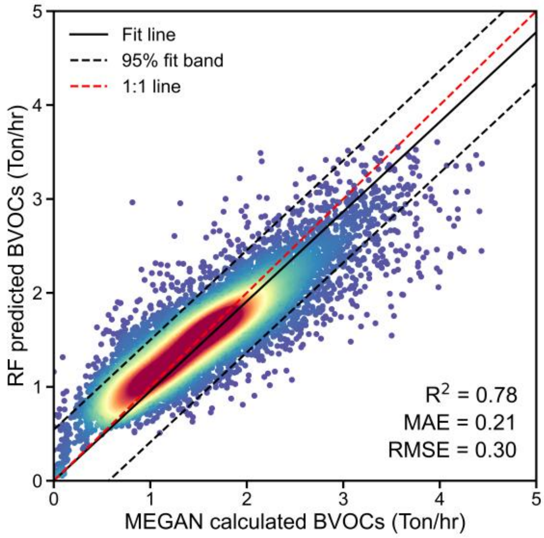

Fig S1 Evaluation of Random Forest model using a 10-fold cross-validation

2. **Figure 4 presents the spatial distribution of sensitivity coefficients for ozone formation with respect to BVOCs. It is suggested that the authors include a percentage difference plot to more intuitively display the influence of BVOC emissions on the spatial distribution of sensitivity coefficients. Additionally, incorporating comparative charts for different years would better illustrate the long-term trends.**

Reply: Thanks for the suggestions. Please note that the O_3 sensitivity coefficient could be zero in some grids in both the AVOC_ONLY and Add_BVOC scenarios, making percentage calculations undefined in these cases, which means it is impossible to provide **a percentage difference plot**. However, as suggested by the reviewer, we have added a **difference plot** between the AVOC_ONLY scenario and the Add_BVOC scenario. Hopefully, the revised Figure 4 could provide a more intuitive representation of the influence of BVOC emissions on the spatial distribution of sensitivity coefficients.

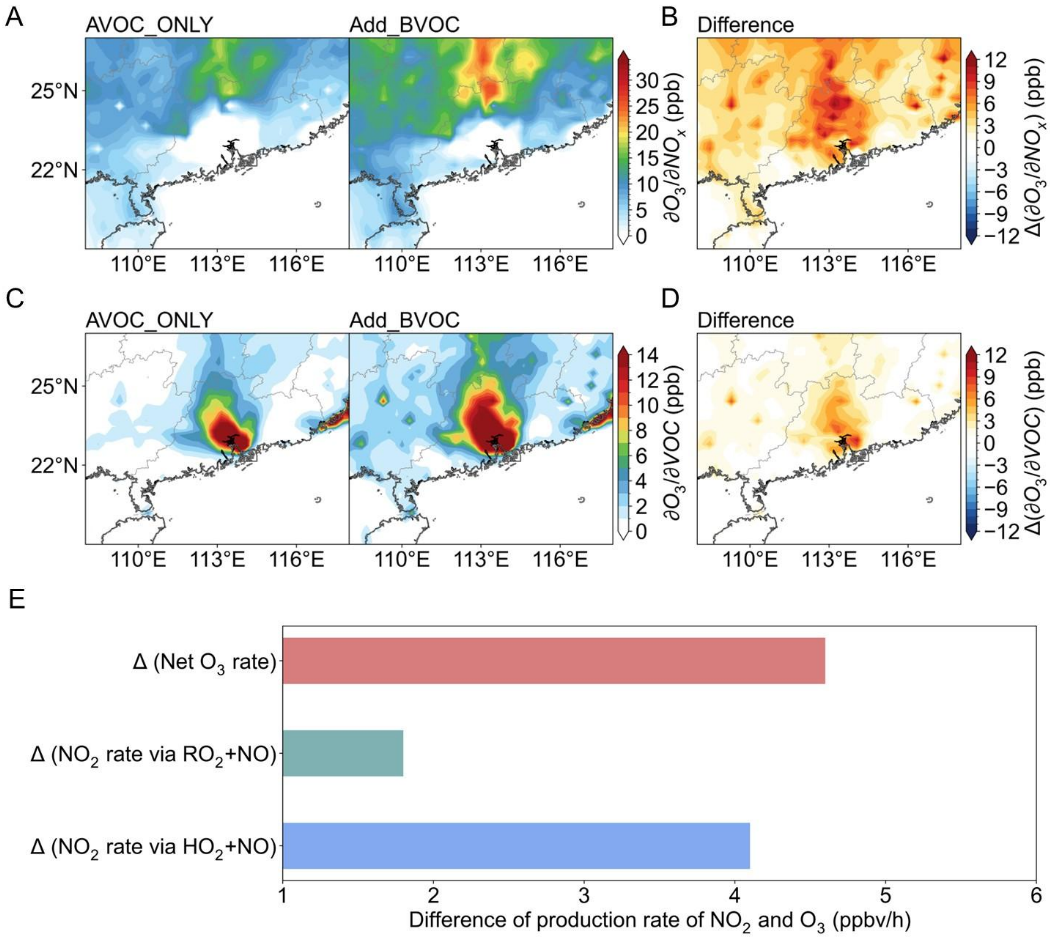

Figure 4. (A) Spatial distribution of O_3 sensitivity coefficients to NO_x emissions under AVOC_ONLY and Add_BVOC scenario. (B) Difference of O_3 sensitivity coefficients to NO_x emissions between Add_BVOC and AVOC_ONLY scenario. (C) Same as (A) but for sensitivity coefficients to VOCs emissions. (D) Same as (B) but for O_3 sensitivity coefficients to VOCs emissions (E) difference of production rate of NO_2 (via chemical pathway of RO_2+NO and HO_2+NO) and net production rate of O_3 at 14:00 between Add_BVOC and AVOC_ONLY scenario

We agree that incorporating comparative charts for different years would better illustrate long-term trends. However, due to the non-linear nature of these responses, the calculations are inherently complex. As you may know, HDDM is a highly computationally intensive model, as it computes O_3 sensitivity coefficients—including first-order, second-order, and higher-order terms—for each precursor (e.g., NO, NO_2, and various VOC species). Running long-term simulations would require extensive computational resources, exceeding the capacity of available supercomputing infrastructure. Moreover, our primary objective is to highlight the significant impact of BVOC emissions on O_3 concentrations. To achieve this, we designed two scenarios:

AVOC_ONLY (considers only anthropogenic VOCs), and ADD_BVOC (accounts for both anthropogenic and biogenic emissions). Both simulations were driven by 2020 meteorological conditions. While comparative charts across multiple years would provide deeper insight into long-term trends, the conclusion regarding the importance of BVOCs emissions on O_3 formation holds true.

3. **The simulation only compares the years 2012 and 2020. This design may not fully capture the dynamic changes in ozone and BVOC emissions from 2001 to 2020, especially since China implemented several significant emission reduction policies between 2012 and 2020, resulting in notable nonlinear changes in ozone concentrations and precursor emissions. Studies, for example, doi.org/10.1038/s41561-023-01284-2, have suggested that the anthropogenic emission reduction in different phases actually led to different impacts on ozone. Did you find the similar results? It will be better to include some intermediate years to illustrate the effects.**

Reply: Thanks for the insightful questions. Indeed, previous studies—including the paper mentioned by the reviewer and our own publications—have already demonstrated that anthropogenic emission reductions at different phases have led to varying impacts on O_3. For instance, our earlier study found that emission control measures during 2012–2017 (Phase One) resulted in increased O_3 levels across most eastern city clusters of China due to NO_x reductions in a VOC-limited regime. In contrast, the reference cited by the reviewer showed that during 2018–2021 (Phase Two), further emission reductions helped mitigate O_3 pollution. These contrasting effects largely stem from shifts in O_3-NO_x-VOCs sensitivity, which have been widely discussed (Wang et al., 2019; Huang et al., 2021; Wang et al., 2023). Our findings align with this pattern, suggesting that nearly a decade of anthropogenic emission control has contributed to a decline in summer O_3 concentrations in the PRD. We did not evaluate year-to-year O_3 responses to emission reductions, as this topic has been extensively studied. To avoid redundancy, our assessment adopts a climatic-scale perspective, examining the anthropogenic controlling influences between 2012 (when anthropogenic emissions reached the peak during the past decade) and the present (2020, almost after a decade of control measures).

Nonetheless, we have added a discussion on O_3 responses to anthropogenic emissions in the manuscript, citing these published studies, "These contrasting effects largely stem from shifts in O_3-NO_x-VOCs sensitivity. Past studies suggested that O_3 levels would temporarily increase in the short term following NO_x emission controls (Wang et al., 2019; Huang et al., 2021). However, after a long-term (nearly a decade) emission reductions, our finding reveals that, when considering only anthropogenic emissions (AVOC_ONLY scenario), emission reductions could lead to varying degrees of O_3 decline in southern China. This result was consistent with a recent study by Wang et al. (2023)"

Moreover, as our primary focus is on biogenic emissions, evaluating the year-by-year impact of anthropogenic emission reductions does not fully align with our research objectives. According to our study, we found BVOCs emissions were kept rising during the past two decades, therefore, we compared their contribution between 2001 and 2020 in order to maxima the contribution of BVOCs to O3 (Please be noted that we didn't only compare the year of 2012 and 2020). Actually, the O_3 formation algorithm we proposed could maximally account for the influences of anthropogenic and biogenic sources to highlight their respective contributions in a climatic scale. (see our revision in lines 243-244)

4. **The authors employed WRF 3.9 and CMAQ 5.3 for the simulations. However, the MCIP module in CMAQ versions 5.2+ does not directly support handling data outputs from WRF versions below 4.0, which may result in data incompatibility or preprocessing errors. Was the MCIP module modified, or was an intermediate data conversion tool used? It should be clearly stated in the manuscript.**

Reply: Thanks for the very technical question. Yes, the MCIP module in CMAQ 5.3 does not directly support data outputs from WRF versions below 4.0. To resolve this issue, we used an earlier version of MCIP (v5.2) to process meteorological data from WRF 3.9. Notably, CMAQ 5.3 remains compatible with MCIP outputs from lower versions (like MCIP v5.2).

Reference

Huang X, Ding A, Gao J, et al. Enhanced secondary pollution offset reduction of primary emissions during COVID-19 lockdown in China[J]. National Science Review, 2021, 8(2): nwaa137.

Wang Y, Zhao Y, Liu Y, et al. Sustained emission reductions have restrained the ozone pollution over China[J]. Nature Geoscience, 2023, 16(11): 967-974.

Wang N, Lyu X, Deng X, et al. Aggravating O3 pollution due to NOx emission control in eastern China[J]. Science of the Total Environment, 2019, 677: 732-744.