Main comments:

In recent years, ozone pollution has become an increasingly serious problem in China. Analyzing the causes of ozone pollution is of great help in its treatment. This study investigated the impact of extreme weather on ozone pollution in the Pearl River Delta, South China, with field measurements, machine learning, and model simulations, and highlighted the significant impact of Natural Processes. The results show that weather-induced natural processes, including meteorological factors, BVOC emissions, STE processes and atmospheric transportations provide substantial contributions to the prolonged O3 pollutions. Particularly, investigation was made upon BVOC chemical pathway with O3 production more attributable to the further degradation of isoprene oxidation products than the direct isoprene oxidation, which presents to be an important mechanism of isoprene contributing to ozone formation. Overall, this study is well organized, and can provide insights for ozone control under global warming. I suggest the paper could be accepted for ACP publication after addressing the following suggestions.

General Response to the reviewer: We would like to thank the reviewer for his/her valuable time in reviewing our manuscript. The comments/suggestions raised do help improve the quality of the study. We have carefully revised the manuscript according to the questions/suggestions, and hope the revision will meet with approval. We have marked the revised in red fonts in the manuscript. Below is the point-to-point response.

Specific comments:

1. Abstract, "isoprene and biogenic formaldehyde accounted for about half of the in-situ O3 production." What's the mean of "about half of the in-situ O3 production"? Does this mean that for ozone production, isoprene and biogenic formaldehyde contributes 50%? How much does the increase in BVOC emissions due to high temperatures affect ozone production compared to normal years? In addition, the conclusion of the article is not clear. The author analyzed the meteorological factors, BVOC emissions, STE processes, and atmospheric transportations, but which one is the most important process?

Reply: Thanks for the interesting questions. Our responses to the questions/suggestions are as follows.

(1) In this study, we used in-situ observations to constrain the F0AM-MCM model (an observation-based photochemical box model, OBM) and simulate the contributions of the precursors to O_3 formation. We found that isoprene and biogenic formaldehyde contributed to 47% O_3 production (about half of the in-situ O_3 production) during the prolonged heatwave.

(2) The in-situ calculation needs observed data (i.e., VOCs species) as input to drive the box model. The field campaign was carried out at the HZ Base from 1st

Sept. to 30th Sept., 2022. It is a pity that we do not have the VOCs data during normal years (such as the same period in 2021 or 2020). So we cannot give a compared result of O_3 production to normal years. However, by using the theorical calculation of BVOC emissions from MEGAN model, we found BVOC emissions increased by 10% due to the extreme weather condition compared to normal years. Compromisingly, we used the ratio of isoprene emissions between 2022 and previous years to scale the observed isoprene in September 2022 in the box model simulation. So, isoprene in the base case was 10% higher than that in the hypothetical case. And it was found that the 10% increase in isoprene contributes an additional O_3 production of 7.5 ppb (OPR of 1.00 ppb h^{-1} at 12:00). Overall, by considering the total impact of BVOC, it was found the contribution to O_3 production rate of BVOC reached 47% (nearly half of the in-situ O_3 production).

(3) According to the result of the study, meteorological factors contribute an additional 10.8 ppb to O_3 levels compared to the same period in previous years; BVOC emissions aggravated photochemical reaction and contributed nearly half of in-situ O_3 production; and STE-induced O_3 contributed to a maximum of ~8 ppb in PRD. Based on the quantified result, BVOC emissions were the most important natural factor in this study. We have modified the abstract by highlighting the dominant role of BVOC, and slightly reorganized the sentences according to the order of the importance.

2. Page 3, Line 66, Change “biogenic volatile carbon” to “biogenic volatile organic compound”

Reply: Thanks. We have corrected it to “biogenic volatile organic compound”.

3. Page 3, Line 66, The author sometimes uses “BVOC” and sometimes uses “BVOCs” in the manuscript, please unify the abbreviation of “BVOC” throughout the text.

Reply: Thanks for the suggestion. We have use “BVOC” throughout the text.

4. Page 3, Line 70-75, Suggesting additional references in these sentences, for example, Lyu et al. (2023), https://doi.org/10.1016/j.oneear.2023.07.004.

Reply: Thanks for the suggestion. We have added the reference.

5. In Section 2.1, please provide the time period of the field campaign at the HZ base.

Reply: OK. We have added the following sentence here, “All the data are collected at the HZ Base from Sept. 1st to Sept. 30th, with a time resolution of 1 hour.”

6. Page 5, Line 127, how was the “regional O3 exceedance” defined?

Reply: In this study, we used the 90th percentile of the maximum daily 8-hour average (MDA8-90) O_3 concentration among 56 monitoring sites distributed in PRD to assess the regional degree of O3 pollution. A regional O_3 exceedance occurs when the MDA8-90 exceeds the China’s Grade II standard (i.e., 160 μg/m^3).

These descriptions have been added in the text now.

7. Page 5, Line 151, Please give more detailed introduction of the detection of VOC species, i.e., how many species?

Reply: Thanks for the suggestions. Please see our revisions, “the target compounds of the instrument were the 56 VOCs designated as photochemical precursors by the US Environmental Protection Agency (EPA). The gas standards utilized were identical to those employed by the US EPA Photochemical Assessment Monitoring Stations (PAMS). More details were documented in our previous paper (Zou et al., 2015).”

8. In Section 2.3, 2.4 and 2.5, when you introduce the model of LPDM, MEGAN and the F0AM, please provide the official website of the model if it is available.

Reply: Thanks for the suggestion. We now have provided the websites in the manuscript now.

9. Page 8, Line 229, “WRF-CMAQ” or “WRF” here? Line 231, which one does "the model" refer to?

Reply: It’s “WRF-CMAQ” here. We have changed “the model” to “WRF-CMAQ”.

10. Page 9, The author compared the model simulated O3 with AIRS data. In addition to the direct objective comparison analysis, it is suggested to provide a statistical result of the comparison, for example, what’s the correlation coefficient between them?

Reply: Thanks for the suggestion. We have added an additional figure in the supplementary file by comparing AIRS data with CAM-Chem simulations in Eastern China (Fig. S3). The following discussion was added in the text, “It was found that the correlation coefficient in Eastern China was 0.79, passed a 95% significance test, indicating the CAM-Chem model relatively well produced O_3 at higher levels.”

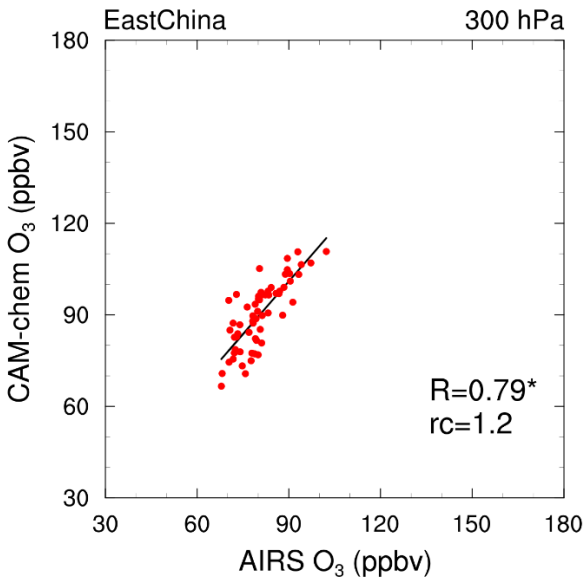

Fig. S3 Validation of AIRS O_3 and CAM-Chem simulated O_3 at 300hPa in Eastern China (R indicates correlation coefficient; rc indicates regression coefficient;* indicates the correlation coefficient has passed a 95% significance test)

11. Page 12, Lines 357-368, This part needs to be compared to the normal years? BVOC emissions increased by 10% compared to the normal years, how about its contribution to O3 production?

Reply: This question is similar with the above one the reviewer has already raised. It was found that the 10% increase in isoprene contributes an additional O_3 production of 7.5 ppb (OPR of 1.00 ppb h-1 at 12:00). We have modified the manuscript by addressing the following sentence, “It was simulated that the 10% increase in isoprene would lead to an additional O3 production of 7.5 ppb (OPR of 1.00 ppb h-1 at 12:00).”

12. BVOC emissions are important natural sources of ambient O3, the author could use a few words to discuss the diurnal characteristics of isoprene measured at HZ base.

Reply: Thanks for the question. We have added the following revision, “Besides, the in-situ observed isoprene exhibited a significant concentration difference between day and night, i.e., 0.52 – 1.25 ppb during 6:00 – 17:00 and an average of 0.10 ppb at other times (Fig. S6)”

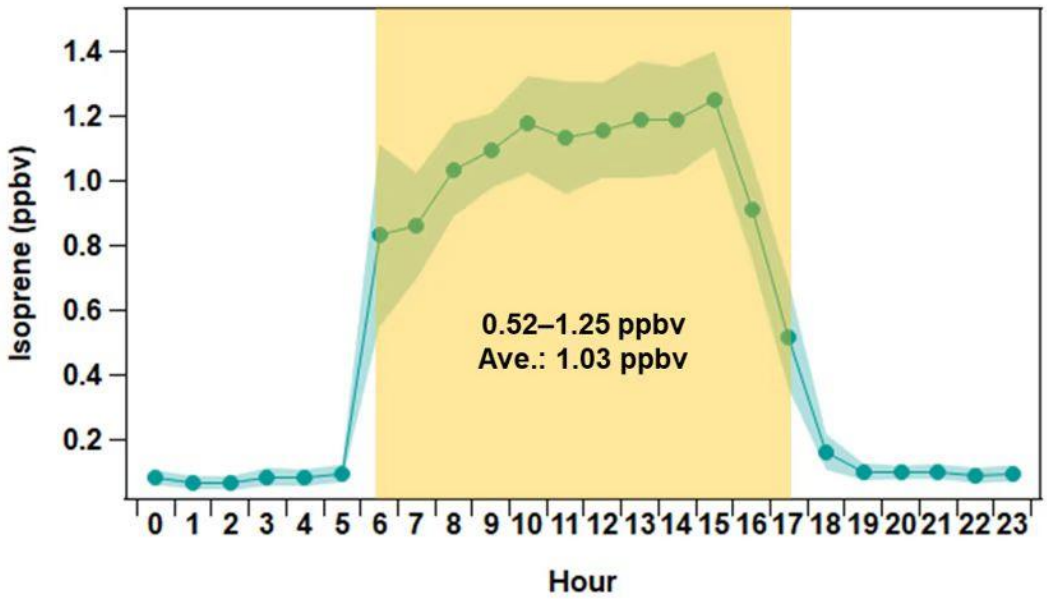

Figure S6 Diurnal variation of isoprene concentrations at HZ Base. (The yellow shaded highlights the daytime averaged concentrations, 0.51-1.25 ppbv. The daily averaged concentration was 1.03 ppbv.)

13. Why you use 10% hypothetical case to simulate the isoprene chemical pathway?

Reply: This increment was based on the result of MEGAN calculations on BVOC emissions. The calculations found that the extreme weather conditions in 2022 led to 10% increase in BVOC emissions compared to normal years.

14. Page 13 “Hence, the impacts of BVOC oxidation intermediates on downwind air quality warrant more attention” this conclusion also needs references to support.

Reply: Thanks for the advice. References were added, “Hence, the impacts of BVOC oxidation intermediates on downwind air quality warrant more attention (Dreyfus et al., 2002; Lee et al., 2014).”

15. Figure 4, it is interesting to see that the authors provide the detailed chemical pathway of isoprene chemistry. I suggest that the author improve the figure by adding a quantified result of how much contribution is from isoprene direct contribution to O3 and how much contribution is via the further degradation of early generation isoprene oxidation products to O3.

Reply: Very good advice. We have amended the figure by adding the contribution of isoprene direct oxidation and further degradation to O_3, respectively. Please see the revised figure.

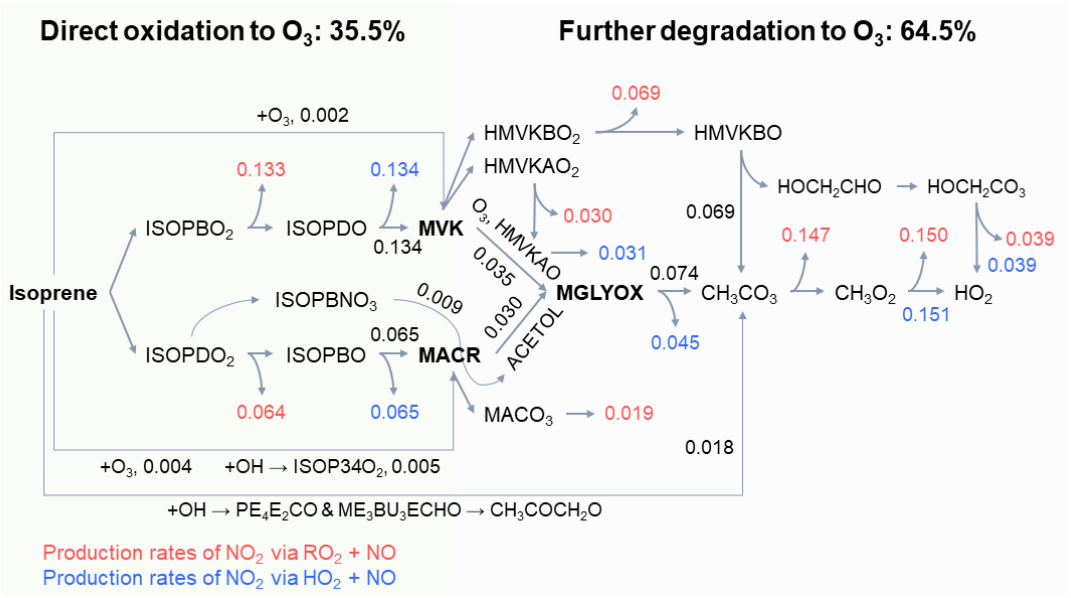

Figure 4 Changes in the rates (numbers; unit: ppbv h^{-1}) of major reactions leading to O_3 formation at 12:00 induced by 10% increase in isoprene concentrations. Red and blue fonts indicate the production rates of NO_2 (via RO_2 + NO) and HO_2, respectively. Abbreviations of the species conform to the MCM naming convention (http://chmlin9.leeds.ac.uk/MCMv3.3.1/home.htt).

16. "STE" has already defined in the previous texts, so you should use "STE" here, instead of using "stratosphere-to-troposphere exchange". Attentions should be paid in similar places throughout the manuscript.

Reply: Thanks. We revised it as suggested.

17. In the Section of Conclusion, it is suggested to provide the quantified contribution of BVOC emissions to O3 formation. So that readers could clearly get the main result of the study.

Reply: Thanks for the good suggestion. "BVOC emissions aggravated photochemical reaction and contributed nearly half of in-situ O_3 production" was added here.

18. In the caption of Figure 2, please define the abbreviation of T2, BLH, RH, WS, U10, w, U850, TCC, V10 and V850

Reply: Thanks. We have revised them in the caption. "Contributions of multi-meteorological factors (2m temperature (T2), boundary layer height (BLH), relative humidity (RH), wind speed (WS), 10 m u-component of wind (U10), w (vertical wind speed), 850 hPa u-component of wind (U850), total cloud coverage (TCC), 10m V-component of wind (V10), and 850hPa V-component of wind (V850)) to O3 in the September of 2022 and 2019-2021"

19. In Figure 3, the caption "HCHO (B_HCHO)" should be "biogenic HCHO (B_HCHO)".

Reply: Yes, thanks for the advice. We have changed it to "biogenic HCHO

(B_HCHO)".

20. In the caption of Figure 7, please define the abbreviation of ISOP, MVK and MARC

Reply: ISOP, MVK and MACR refer to isoprene, methyl vinyl ketone and methacrolein, respectively.

References

Dreyfus, G. B., Schade, G. W., and Goldstein, A. H.: Observational constraints on the contribution of isoprene oxidation to ozone production on the western slope of the Sierra Nevada, California, Journal of Geophysical Research: Atmospheres, 107, ACH 1-1-ACH 1-17, 2002.

Lee, K.-Y., Kwak, K.-H., Ryu, Y.-H., Lee, S.-H., and Baik, J.-J.: Impacts of biogenic isoprene emission on ozone air quality in the Seoul metropolitan area, Atmospheric Environment, 96, 209-219, 2014.

Zou, Y., Deng, X., Zhu, D., Gong, D., Wang, H., Li, F., Tan, H., Deng, T., Mai, B., and Liu, X.: Characteristics of 1 year of observational data of VOCs, NO x and O 3 at a suburban site in Guangzhou, China, Atmospheric Chemistry and Physics, 15, 6625-6636, 2015.