Response to Reviewer 1

General Comments:

The manuscript, titled “Extreme Weather’s Impact on Ozone Pollution in China,” investigates Ozone (O$_3$) pollution in China, emphasizing the overlooked role of natural processes. It analyzes the effects of extreme weather events in the September 2022 Pearl River Delta (PRD) case, which led to prolonged high O$_3$ levels and extreme temperatures due to the Subtropical High and typhoon peripheries. Using field measurements, machine learning, and numerical modeling, the study examines the influence of weather-induced natural processes on O$_3$ pollution. Findings indicate that hot weather intensifies photochemical reactions, adding 10.8 ppb of O$_3$ compared to standard conditions, with temperature as the primary factor. The study also highlights the role of biogenic volatile organic compounds, particularly isoprene, in O$_3$ production. Additionally, it explores the chemical mechanisms behind isoprene’s contribution. Notably, a nearing typhoon enhances cross-regional O$_3$ transport via stratosphere-to-troposphere exchange (STE). Model simulations suggest STE-induced O$_3$ reaching a maximum of approximately 8 ppb at the PRD surface. In summary, the study underscores the significant impact of natural processes exacerbated by extreme weather on O$_3$ pollution and offers insights for O$_3$ pollution control amidst global warming. Overall, the study is well-structured and provides valuable insights into the topic. However, there are some areas that require attention before publication. Therefore, I would recommend acceptance to this manuscript after the following minor revisions were made and the questions were answered.

General Response to the reviewer 1: Thank you very much for your valuable comments and suggestions. Your positive comments/suggestions have motivated us to improve the manuscript. Now, we have carefully revised the manuscript based on all your questions/suggestions, and hope the correction will meet with approval. We have marked the revised sentences in red color in the manuscript. Below is the point-to-point response.

Specific Comments:

1. Page 3, Line 60: The phrase "sun-light driven" should be corrected to "sunlight-driven."

Reply: Thanks for the careful reminder. We have revised it as suggested.

2. Page 3, Line 66 & 86: The phrase "biogenic volatile carbon" should be corrected to "biogenic volatile organic compound". And please unify the abbreviation of “BVOC”.

Reply: Thanks for pointing out our mistakes. We have changed them to “biogenic volatile organic compound”. And we also unified the abbreviation of BVOC throughout the manuscript.

3. Page 3, Line 88: Abbreviation of “HOx” should be defined.

Reply: Thanks for the careful review. Abbreviation of HOx is now defined, hydrogen oxide (HOx) radicals.

4. Page 4, Line 101: The phrase “nature processes” should be corrected to “natural processes”.

Reply: Thanks. We revised the phrase “nature processes” to “natural processes” as.

5. Page 4, Line 105: Abbreviation of “CO” should be defined.

Reply: Revised as suggested. The phrase is corrected to “carbon monoxide (CO)”

6. Page 4, Line 107-109: After a semicolon (;), the following word should typically start with a lowercase letter, therefore, “Vegetation-released” and “An” should change to “vegetation-released” and “an”.

Reply: Thanks. We now used lowercase letter as suggested.

7. Page 4, Line 109: The phrase “largescale” should be corrected to “large-scale”.

Reply: Revised as suggested.

8. According to the ACP’s submission guide to author, the abbreviation “Fig.” should be used when it appears in running text and should be followed by a number unless it comes at the beginning of a sentence. Labels of panels must be included with brackets around letters being lower case (e.g. (a), (b), etc.).
   a. Page 5, Line 137: “Figure 1a” should be “Fig. 1(a)”. 
   b. Page 6, Line 161: “Figure 1a” should be “Fig. 1(a)”. 
   c. Page 7, Line 198: “Figure S1” should be “Fig. S1”. 
   d. Page 9, Line 272: “Figure S2” should be “Fig. S2”. 
   e. Page 9, Line 280: “Figure S3” should be “Fig. S3”. 
   f. Page 9, Line 293: “Figure 1b” should be “Fig.1(b)”. 
   g. Page 10, Line 298: “Figure S4” should be “Fig. S4”. 
   h. Page 10, Line 300: “Figure 1b” should be “Fig. 1(b)”. 
   i. Page 10, Line 303: “Figure 1c” should be “Fig. 1(c)”. 
   j. Page 10, Line 305: “Figure 1c” should be “Fig. 1(c)”. 
k. Page 10, Line 313: “Figure 1d” should be “Fig. 1(d)”.
l. Page 10, Line 323: “Figure 2” should be “Fig. 2”.
m. Page 12, Line 355: “Figure 3a” should be “Fig. 3(a)”.
n. Page 12, Line 359: “Figure 3b” should be “Fig. 3(b)”.
o. Page 13, Line 381: “Figure 4” should be “Fig. 4”.
p. Page 14, Line 419: “Figure S5” should be “Fig. S5”.
q. Page 14, Line 425: “Figure S5” should be “Fig. S5”.
r. Page 14, Line 433: “Figure 5a” should be “Fig. 5(a)”.
s. Page 14, Line 436: “Figure 5b” should be “Fig. 5(b)”.
t. Page 14, Line 441: “Figure S6” should be “Fig. S6”.
u. Page 14, Line 445 “Figure 5b” should be “Fig. 5(b)”.
v. Page 14, Line 446 “Figure 5c” should be “Fig. 5(c)”.
w. Page 14, Line 446 “Figure 5d” should be “Fig. 5(d)”.
x. Page 15, Line 450 “Figure 5e” should be “Fig. 5(e)”.
y. Page 15, Line 451 “Figure 5f” should be “Fig. 5(f)”.
z. Page 15, Line 454 “Figure S7-S9” should be “Fig. S7-S9”.

Reply: We appreciate so much for the careful review. We have consistently employed the abbreviation “Fig.” throughout the text. Besides, labels of panels are also included with brackets around letters being lower case.

9. Page 5, Line 144:

a. In the sentence “meteorological parameters (surface winds, temperature and solar radiation)”, some meteorological parameters including precipitation and relative humidity were not mentioned.

Reply: Thanks for the reminder. We added relative humidity, and precipitation here.

b. When and for how long were online observations conducted for O3, NOx, SO2, CO, VOC components, and meteorological parameters at this observation base?

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

10. Page 5, Line 151: What and how many VOC species were measured?

Reply: The instrument could detect 56 volatile VOCs species (Table R1). We added the following description here “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).”
Table R1* The calibration curves and detection limits of VOC species

<table>
<thead>
<tr>
<th>Target compound</th>
<th>Calibration curve</th>
<th>Correlation coefficient</th>
<th>Detection limit (ppbv)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethane</td>
<td>$y = 1.0188x + 0.2659$</td>
<td>0.997</td>
<td>0.07</td>
</tr>
<tr>
<td>Acetylene</td>
<td>$y = 1.0409x + 0.1756$</td>
<td>0.998</td>
<td>0.08</td>
</tr>
<tr>
<td>Ethane</td>
<td>$y = 1.0162x + 0.2891$</td>
<td>0.997</td>
<td>0.08</td>
</tr>
<tr>
<td>Propene</td>
<td>$y = 0.9959x + 0.1506$</td>
<td>0.999</td>
<td>0.07</td>
</tr>
<tr>
<td>Propane</td>
<td>$y = 0.9834x + 0.2682$</td>
<td>0.998</td>
<td>0.09</td>
</tr>
<tr>
<td>1-Butene</td>
<td>$y = 0.9753x + 0.3785$</td>
<td>0.994</td>
<td>0.05</td>
</tr>
<tr>
<td>n-Butane</td>
<td>$y = 0.9776x + 0.3718$</td>
<td>0.994</td>
<td>0.05</td>
</tr>
<tr>
<td>trans-2-Butene</td>
<td>$y = 0.9746x + 0.2747$</td>
<td>0.997</td>
<td>0.05</td>
</tr>
<tr>
<td>cis-2-Butene</td>
<td>$y = 0.9834x + 0.1606$</td>
<td>0.999</td>
<td>0.06</td>
</tr>
<tr>
<td>i-Pentene</td>
<td>$y = 0.9753x + 0.2135$</td>
<td>0.998</td>
<td>0.07</td>
</tr>
<tr>
<td>1-Pentene</td>
<td>$y = 0.919x + 0.1626$</td>
<td>0.998</td>
<td>0.05</td>
</tr>
<tr>
<td>n-Pentane</td>
<td>$y = 0.9557x + 0.2038$</td>
<td>0.984</td>
<td>0.07</td>
</tr>
<tr>
<td>Isoprene</td>
<td>$y = 1.0304x - 0.1653$</td>
<td>0.998</td>
<td>0.07</td>
</tr>
<tr>
<td>trans-2-pentene</td>
<td>$y = 0.9753x + 0.2135$</td>
<td>0.998</td>
<td>0.07</td>
</tr>
<tr>
<td>cis-2-pentene</td>
<td>$y = 0.9557x + 0.2038$</td>
<td>0.984</td>
<td>0.07</td>
</tr>
<tr>
<td>2,2-Dimethylbutane</td>
<td>$y = 0.9731x + 0.1971$</td>
<td>0.998</td>
<td>0.07</td>
</tr>
<tr>
<td>Cyclopentane</td>
<td>$y = 0.9993x + 0.1412$</td>
<td>0.997</td>
<td>0.06</td>
</tr>
<tr>
<td>2,3-Dimethylbutane</td>
<td>$y = 0.919x + 0.1626$</td>
<td>0.999</td>
<td>0.07</td>
</tr>
<tr>
<td>2-Methylpentane</td>
<td>$y = 0.9578x + 0.2038$</td>
<td>0.984</td>
<td>0.07</td>
</tr>
<tr>
<td>3-Methylpentane</td>
<td>$y = 0.9753x + 0.2135$</td>
<td>0.998</td>
<td>0.07</td>
</tr>
<tr>
<td>1-Hexene</td>
<td>$y = 0.9700x + 0.3300$</td>
<td>0.993</td>
<td>0.06</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>$y = 0.9915x - 0.2626$</td>
<td>0.998</td>
<td>0.06</td>
</tr>
<tr>
<td>Methylcyclopentane</td>
<td>$y = 0.9749x + 0.1832$</td>
<td>0.999</td>
<td>0.07</td>
</tr>
<tr>
<td>2,4-Dimethylpentane</td>
<td>$y = 0.9993x + 0.1412$</td>
<td>0.999</td>
<td>0.05</td>
</tr>
<tr>
<td>Benzene</td>
<td>$y = 0.9753x + 0.2835$</td>
<td>0.997</td>
<td>0.06</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>$y = 0.9841x + 0.2744$</td>
<td>0.997</td>
<td>0.07</td>
</tr>
<tr>
<td>2-Methylhexane</td>
<td>$y = 0.9744x + 0.2979$</td>
<td>0.996</td>
<td>0.05</td>
</tr>
<tr>
<td>2,3-Dimethylpentane</td>
<td>$y = 0.9779x + 0.2953$</td>
<td>0.997</td>
<td>0.05</td>
</tr>
<tr>
<td>3-Methylhexane</td>
<td>$y = 0.9735x + 0.3374$</td>
<td>0.993</td>
<td>0.06</td>
</tr>
<tr>
<td>2,2,4-Trimethylpentane</td>
<td>$y = 0.9666x + 0.3947$</td>
<td>0.994</td>
<td>0.05</td>
</tr>
<tr>
<td>n-Heptane</td>
<td>$y = 0.9678x + 0.3635$</td>
<td>0.994</td>
<td>0.05</td>
</tr>
<tr>
<td>Methylcyclohexane</td>
<td>$y = 0.9819x + 0.3629$</td>
<td>0.995</td>
<td>0.05</td>
</tr>
<tr>
<td>2,3,4-Trimethylpentane</td>
<td>$y = 0.9691x + 0.3994$</td>
<td>0.994</td>
<td>0.05</td>
</tr>
<tr>
<td>Toluene</td>
<td>$y = 0.9696x + 0.3397$</td>
<td>0.995</td>
<td>0.05</td>
</tr>
<tr>
<td>2-Methylpentane</td>
<td>$y = 0.9603x + 0.4835$</td>
<td>0.990</td>
<td>0.04</td>
</tr>
<tr>
<td>3-Methylpentane</td>
<td>$y = 0.9825x + 0.4550$</td>
<td>0.991</td>
<td>0.04</td>
</tr>
<tr>
<td>n-Octane</td>
<td>$y = 0.9524x + 0.3082$</td>
<td>0.989</td>
<td>0.04</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>$y = 0.9629x + 0.4253$</td>
<td>0.992</td>
<td>0.04</td>
</tr>
<tr>
<td>n-, p-Xylenes</td>
<td>$y = 0.9541x + 0.5844$</td>
<td>0.986</td>
<td>0.03</td>
</tr>
<tr>
<td>Styrene</td>
<td>$y = 0.9524x + 0.4132$</td>
<td>0.991</td>
<td>0.04</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>$y = 0.9515x + 0.4926$</td>
<td>0.989</td>
<td>0.04</td>
</tr>
<tr>
<td>n-Octane</td>
<td>$y = 0.9878x + 0.1635$</td>
<td>0.998</td>
<td>0.04</td>
</tr>
<tr>
<td>t-Propylbenzene</td>
<td>$y = 0.9418x + 0.5162$</td>
<td>0.986</td>
<td>0.04</td>
</tr>
<tr>
<td>n-Propylbenzene</td>
<td>$y = 0.9426x + 0.5468$</td>
<td>0.986</td>
<td>0.04</td>
</tr>
<tr>
<td>m-Ethyltoluene</td>
<td>$y = 0.9532x + 0.4838$</td>
<td>0.989</td>
<td>0.04</td>
</tr>
<tr>
<td>p-Ethyltoluene</td>
<td>$y = 0.9554x + 0.3953$</td>
<td>0.992</td>
<td>0.04</td>
</tr>
<tr>
<td>1,3,5-Trimethylbenzene</td>
<td>$y = 0.951x + 0.4724$</td>
<td>0.989</td>
<td>0.04</td>
</tr>
<tr>
<td>o-Ethylbenzene</td>
<td>$y = 0.9784x + 0.0956$</td>
<td>0.999</td>
<td>0.03</td>
</tr>
<tr>
<td>1,2,4-Trimethylbenzene</td>
<td>$y = 0.9563x + 0.4509$</td>
<td>0.991</td>
<td>0.03</td>
</tr>
<tr>
<td>n-Decane</td>
<td>$y = 0.9651x + 0.3068$</td>
<td>0.995</td>
<td>0.04</td>
</tr>
<tr>
<td>1,2,3-trimethylbenzene</td>
<td>$y = 0.9537x + 0.3191$</td>
<td>0.993</td>
<td>0.04</td>
</tr>
<tr>
<td>m-Diethylbenzene</td>
<td>$y = 0.9541x + 0.4494$</td>
<td>0.991</td>
<td>0.04</td>
</tr>
<tr>
<td>p-Diethylbenzene</td>
<td>$y = 0.9607x + 0.3788$</td>
<td>0.993</td>
<td>0.04</td>
</tr>
<tr>
<td>n-Undecane</td>
<td>$y = 0.9519x + 0.3329$</td>
<td>0.992</td>
<td>0.04</td>
</tr>
<tr>
<td>n-Dodecane</td>
<td>$y = 0.9890x + 0.2711$</td>
<td>0.993</td>
<td>0.05</td>
</tr>
</tbody>
</table>

11. Page 6, Line 161: The word "site" should be corrected to "sites".

Reply: Revised as suggested.

12. Page 7, Line 199:

a. Please clarify R (state clearly whether it is Pearson correlation coefficient or coefficients of determination) and the calculation of p-Value (from one-tail or two-tailed t-test).

Reply: Please see our modifications, “Pearson correlation coefficient (R) = 0.84 and p-Value (from two-tailed t-test) < 0.01”

b. R>0.84 should be “R = 0.84” as stated in Fig. S1

Reply: Thanks again for pointing out our mistake. We corrected it to “Pearson correlation coefficient (R) = 0.84”.

13. Page 7, Line 207: Please explain and elaborate how 3000 particulates were released at 100 m above sea level (a.s.l) over the site (HZ Base) and how their backward movement was tracked for 48 hours with a time resolution of 1 hour.

Reply: For the former question, these are the input configurations of the LPDM model, namely, we used 3000 particulates at 100m over the site. The reason we choose 100m a.s.l instead of ground level is to avoid the block effect of buildings/constructions, so that the simulated air masses could correctly represent the region’s information. For the latter question, the calculation of the backward movement was using the HTSPLIT model. Generally, the calculation is a hybrid between the Lagrangian approach, using a moving frame of reference for the advection and diffusion calculations as the trajectories or air parcels move from their initial location, and the Eulerian methodology, which uses a fixed three-dimensional grid as a frame of reference to compute pollutant air concentrations.

14. Page 7, Line 218: The format of the end-text citation “(Guenther et al. (2012)” was not correct. It should be changed to “(Guenther et al., 2012)”.

Reply: Thanks. We changed it to “(Guenther et al., 2012)”.

15. Page 7, Line 225: “Moderate-Resolution Imaging Spectroradiometer” should appear before its abbreviation “MODIS”. Therefore, “MODIS (Moderate-Resolution Imaging Spectroradiometer)” should be corrected to “Moderate-Resolution Imaging Spectroradiometer (MODIS)”.

Reply: Thanks. We corrected it as suggested.
16. Page 8, Line 229: “Weather Research Forecast-Community Multi Scale Air Quality” should appear before its abbreviation “WRF-CMAQ”. Therefore, “WRF-CMAQ (Weather Research Forecast-Community Multi Scale Air Quality)” should be corrected to “Weather Research Forecast-Community Multi Scale Air Quality (WRF-CMAQ)”.

Reply: Thanks. We corrected it as suggested.

17. Page 8, Line 233: Please explain why the meteorological fields of 2019-2021 were used as a parallel simulation of that in September 2022. Why only applied the data from previous three years but not four/five years?

Reply: Thanks for the interesting question. Our objective is to emphasize the extreme high temperatures of September 2022. To achieve this, we sought to compare the data for September 2022 with past averages. Yes, we did conduct a comparison using temperature data for different historical periods, namely, 2019-2021 (three years), 2018-2021 (four years), and 2017-2021 (five years). The resulting average temperatures for these periods were 31.5°C, 31.3°C, and 31.4°C, respectively. Given the relatively minor fluctuations in the temperature moving averages over the past few years, we believe that all these moving averages could highlight the exceptional high temperatures in September 2022. Considering that the use of computing resources would increase with more years considered, we opted for the meteorological data from 2019-2021. This decision does not compromise the primary goal of our study (to highlight the extreme high temperature in 2022 September).

18. Page 8, Line 241-242: In-text citation should be used in this sentence, it is suggested to be changed to “The application method was roughly in line with that in Lyu et al. (2022).”

Reply: Thanks. We corrected it to “The application method was roughly in line with that in Lyu et al. (2022).”

19. Page 8, Line 243: Abbreviation of “SO2” should be defined.

Reply: Revised as suggested.

20. Page 8, Line 248: Abbreviations of “NO” and “NO2” should be defined.

Reply: We defined as the following “A ‘family conservation’ that set the total NOx to the observed value every hour and allowed nitrogen monoxide (NO) and nitrogen dioxide (NO2) to evolve over time was applied.”

21. Page 8, Line 256: The word “exacted” should be replaced by “extracted”.

Reply: We replaced it with “extracted”.
Reply: Thanks for the careful review, we corrected it to “extracted”.

22. Page 9, Line 262: Abbreviation of “NCAR” should be defined.
Reply: We corrected it to “National Center for Atmospheric Research (NCAR)”

23. Page 9, Line 263-264: Abbreviation of “STE” has already mentioned once in the previous content, so “STE” should be used instead of “stratosphere-to-troposphere exchange”.
Reply: Yes. We corrected it to “STE” here.

24. Page 9, Line 265-267: Abbreviations of “MERRA2” and “MOZART-T1” should be defined.
Reply: “National Center for Atmospheric Research (NCAR)” and “Model for Ozone and Related Chemical Tracers (MOZART)” were updated here.

25. Page 9, Line 273-276: Please provide supporting references or evidence for these mentioned uncertainties if any.
Reply: Supporting references are added here. “it was worth noting that the satellite retrievals themselves contain uncertainties, mainly from the impact of clouds, aerosols, surface albedo and the inversion algorithms (Briegleb et al., 1986; De Smedt et al., 2010; Povey and Grainger, 2015)”


26. Page 9, Line 277: It was mentioned that the simulated O3 showed good agreement with the AIRS data. To enhance clarity, could you provide specific details on the extent of this agreement, such as relevant figures or quantitative measures?
Reply: With regard to the suggestion, we 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 O₃ at higher levels.

Fig. S3 Validation of AIRS O₃ and CAM-Chem simulated O₃ at 300hPa in Eastern China (R indicates correlation coefficient; rc indicates regression coefficient)

Besides, we also compared the surface O₃ levels between the in-situ observation and the model simulation as demonstrated in Fig. S4. The daily magnitude and variation trend were successfully captured in Guangzhou, with a mean bias error (MBE) of -7.9 ppb and a root mean square error (RMSE) of 16.3 ppb. Given the relatively well performance of CAM-Chem in both high levels and the surface level, we believe that the results could be accepted for further analyses.

27. Page 9, Line 284: The word “have” should be changed to “has” if only one paper is included.

Reply: Revised as suggested.

28. Page 9, Line 293: The word “concentration” should be changed to “concentrations”.

Reply: Thanks. We changed it to “concentrations”

29. Page 12, Line 355: It was mentioned that there is a significant concentration difference in in-situ observed isoprene between day and night. Could you please provide the specific data and, if available, relevant figures to illustrate the significance of this difference?

Reply: Thanks for the suggestion. During the daytime (6:00 – 17:00), the in-situ observed isoprene concentration ranged between 0.52 – 1.25 ppb, while at other
times, the average concentration was 0.1 ppb. The description was documented in the manuscript “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.)

30. Page 12, Line 369: Please specify the figure you are referencing in this section.

Reply: Revised as suggested.

31. Page 13, Line 408: Abbreviation of “STE” has already mentioned once in the previous content, so “STE” should be used instead of “stratosphere-to-troposphere exchange”.

Reply: Thanks. We have made this modification as suggested.

32. Page 14, Line 427: Abbreviation of “PRD” has already mentioned once in the previous content, so “PRD” should be used instead of “Pearl River Delta”.

Reply: Yes, we changed it to “PRD”.

33. Page 14, Line 433: Abbreviation of “PV” has already mentioned once in the previous content, so “PV” should be used instead of “potential vorticity”.

Reply: Thanks. We have made this modification as suggested.

34. Page 14, Line 445: For consistency, the term “dry air” should be replaced with “specific humidity”, which was mentioned in fig. 5(c).

Reply: We replaced “dry air” with “low specific humidity”.

35. Page 15, Line 453: Similar patterns were consistently observed on other days between September 13-16, 2022 (Figure S7-S9), however, figures corresponding to September 14, 2022, appears to be missing in the appendix.

Reply: Sorry for the misunderstanding. The figure corresponding to September 14, 2022 was provided in Fig. 5 in the manuscript. We now have specified the date in the manuscript. “According to Fig. 5(a), a notable high value of PV was observed in eastern China, specifically spanning from the North China Plain (NCP) area to southern China on September 14, 2022.”. Also, the date information is also included in the caption of Fig. 5.

36. Page 15, Conclusion and implication: It appears that meteorological factors, natural emissions, chemistry pathways, and atmospheric transport each contribute to O3 pollution in this study. Could you please provide numerical quantifications for the contribution of each factor?

Reply: Thanks for the good suggestion. Since the methods we use to study the impact of these factors on O3 concentrations are founded on different principles, for example, the contribution from meteorology are based on machine learning methods, the contribution from natural emissions are based on in-situ observation constrained box model calculations, and the contributions of atmospheric transport are from a chemical transport model simulations, it is inappropriate to perform a closed calculation of the contributions quantified based on different principles. However, we tried to improve the writing by providing numerical quantifications for the contribution of each factor in the Conclusion and Implication Part. For the meteorological contribution, “we identified that meteorological factors contribute an additional 10.8 ppb to O3 levels compared to the same period in previous years” (Page 15); for the impact of BVOCs, “hot weather stimulated BVOC emissions (increased by 10%)” (Page 15) and “BVOC emissions aggravated photochemical reaction and contributed nearly half of in-situ O3 production” (Page 16); for the contribution by atmospheric transportation, “This process resulted in a non-negligible contributor to the surface levels in downwind area (such as the PRD, reached a maximum of ~ 8 ppb)” (Page 16).

37. Page 17, Line 517: In Figure 1(c), Please specify the time frame or date range for the distribution of 500 hPa pressure and winds.
Reply: The illustration has been changed to “Distribution of 500 hPa pressure and winds of September 2022.”

38. Page 17, Line 518: In Figure 1(d), Please specify the abbreviations for TEMP, UVB, PRECIP, WS, RH, and BLH for clarity.

Reply: Thanks for the suggestion. We have revised them to “(d) Comparisons of meteorological parameters (temperature (TEMP), precipitation (PRECIP), relative humidity (RH), ultraviolet radiation b (UVB), wind speed (WS) and boundary layer height (BLH)) between 2022 and 2019-2021”

39. Supplementary Materials, Page 5, Figure S3: Please specify the legend keys for “Obs” and “CAM-chem” for clarity.

Reply: We have added the illustration in the caption. “Obs refers to data from observations and CAM-Chem refers to the model simulated result.”

40. Supplementary Materials, Page 11, Table S1: Please capitalize all column names, including 'model' and 'resolution'.

Reply: Thanks for the suggestion, we have capitalized the column names. Please see the revised Table S1.
Response to Reviewer 2

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 2: 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 O3 formation. We found that isoprene and biogenic formaldehyde contributed to 47% O3 production (about half of the in-situ O3 production) during the prolonged heatwave.
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 theoretical 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.


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 O3 exceedance occurs when the MDA8-90 exceeds the China’s Grade II standard (i.e., 160 μg/m³). 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 O3 at higher levels.”
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 O3 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 O3, 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.html).

16. “STE” has already defined in the previous texts, so you should use “STE” here, instead of using “stratosphere-to-troposphere exchange”. Attention 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 O$_3$ 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 O$_3$ 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
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**

