Response to Reviewer 1

General Comments:

The study investigates the mechanism of regional ozone (O3) pollution disparities in the Sichuan Basin during a severe heatwave event. Chengdu experienced a 17-day O3 exceedance, while the O3 levels in Chongqing were below the national standard. It was found that high temperature and solar radiation intensity, as well as the accumulation of pollutants, were the key contributors to the O3 episodes in Chengdu. Meanwhile, model simulations revealed that the O3 formation regime is VOC-sensitive in Chengdu and transitional in Chongqing. As a result, the biogenic volatile organic compounds (BVOCs), especially isoprene, played a significant role in O3 formation in Chengdu, while contributing less in Chongqing, despite its higher emissions. Besides, in comparison with the strong local O3 formation in Chengdu, regional transport influenced the O3 levels in Chongqing predominantly, highlighting the need for targeted pollution control measures on the regional scale. Overall, this manuscript is well-written and of interesting scientific value. However, there are some minor issues and questions that require attention before publication. Therefore, I would recommend acceptance of this manuscript after the following issues are addressed.

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:

In Lines 138-140: More specificity is needed in describing the locations and surroundings of the sampling sites. The authors could also mark their locations in Fig 1 to clarify.

Reply: Thanks for the suggestion. The following descriptions were added in the manuscript to introduce the sampling sites, **"**Data of atmospheric compositions, including O_3, NO_x (NO and NO_2), CO, SO_2, VOCs components and meteorological parameters were collected from two in-situ observational sites. The Chengdu sampling site was located on the rooftop super monitoring station of the Chengdu Environmental Science Academy in Qingyang District, Chengdu (30.65°N, 106.49°E), while the Chongqing sampling site was situated on the rooftop research observation station of Longshan Primary School in Yubei District, Chongqing (29.75°N, 106.46°E). Both sites were situated in mixed-use areas encompassing traffic arteries, commercial, and residential zones, serving as representative locations for assessing urban air quality.**"**

In addition, their locations were also marked in Fig 1 as suggested.

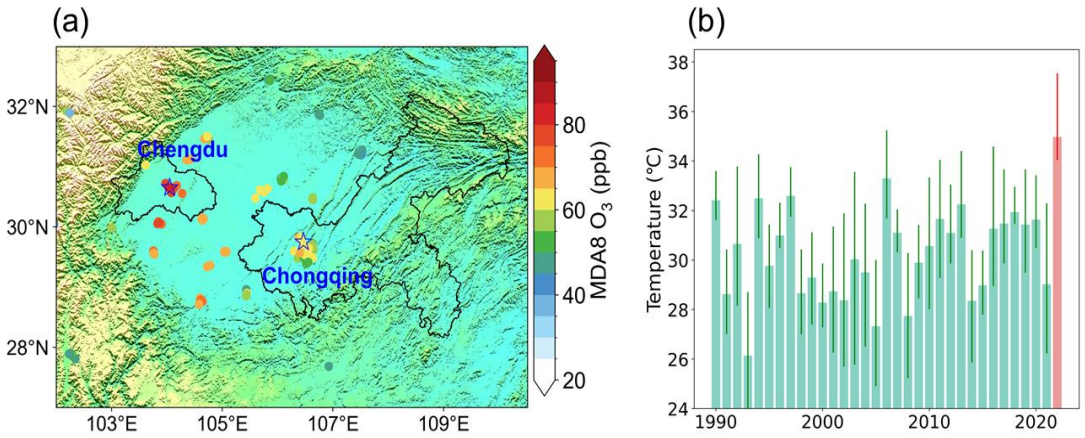


Fig 1 (a) Geographical distribution of Sichuan Basin with scattered averaged monthly MDA8 O_3 concentrations (data obtained from Ministry of Ecology and Environment of China). The black lines highlight the administrative border of Chengdu and Chongqing, respectively. The blue star shows the locations of the supersites. (b) Historical monthly averaged daily-maximum air temperature (August) variation of the SCB from 1990 to 2022. The red bar highlights the extreme hot temperature in 2022.

In Lines 146-147: Online GC instruments were used to measure VOCs. What about the quality control of these instruments, such as the limit of detection, precision, and accuracy?

Reply: The online GC instruments was GC955-611/811（by Synspec）. The instrument targeted the VOCs species designated as photochemical precursors by the US Environmental Protection Agency (EPA). The gas standards used were identical to those employed by the US EPA Photochemical Assessment Monitoring Stations (PAMS). The calibration curves and detection limits of VOCs species were summarized in Table R1.

Table R1* The calibration curves and detection limits of VOC species

Target compound	Calibration curve	Correlation coefficient	Detection limit (ppbv)
Ethene	$y = 1.0188x + 0.2659$	0.997	0.07
Acetylene	$y = 1.0409x + 0.1756$	0.998	0.08
Ethane	$y = 1.0162x + 0.2891$	0.997	0.08
Propene	$y = 0.9959x + 0.1506$	0.999	0.07
Propane	$y = 0.9824x + 0.2082$	0.998	0.09
i-Butane	$y = 0.9753x + 0.3785$	0.994	0.05
1-Butene	$y = 0.9587x + 0.3641$	0.994	0.06
n-Butane	$y = 0.9776x + 0.3718$	0.994	0.05
trans-2-Butene	$y = 0.9746x + 0.2747$	0.997	0.05
cis-2-Butene	$y = 0.9834x + 0.1606$	0.999	0.06
i-Pentane	$y = 0.9753x + 0.2135$	0.998	0.07
1-Pentene	$y = 0.919x + 0.1626$	0.998	0.05
n-Pentane	$y = 0.9557x + 0.2038$	0.984	0.07
Isoprene	$y = 1.0304x + 0.1653$	0.998	0.07
trans-2-pentene	$y = 0.9753x + 0.2135$	0.998	0.07
cis-2-pentene	$y = 0.9557x + 0.2038$	0.984	0.07
2,2-Dimethylbutane	$y = 0.9731x + 0.1971$	0.998	0.07
Cyclopentane	$y = 0.9993x + 0.1412$	0.997	0.06
2,3-Dimethylbutane	$y = 0.919x + 0.1626$	0.999	0.07
2-Methylpentane	$y = 0.9557x + 0.2038$	0.984	0.07
3-Methylpentane	$y = 0.9753x + 0.2135$	0.998	0.07
1-Hexene	$y = 0.9700x + 0.3300$	0.995	0.05
n-Hexane	$y = 0.9915x + 0.2626$	0.997	0.06
Methylcyclopentane	$y = 0.9749x + 0.1832$	0.999	0.07
2,4-Dimethylpentane	$y = 0.9993x + 0.1412$	0.999	0.05
Benzene	$y = 0.9753x + 0.2835$	0.997	0.06
Cyclohexane	$y = 0.9841x + 0.2744$	0.997	0.07
2-methylhexane	$y = 0.9744x + 0.2979$	0.996	0.05
2,3-dimethylpentane	$y = 0.9779x + 0.2953$	0.997	0.05
3-methylhexane	$y = 0.9735x + 0.3374$	0.995	0.05
2,2,4-trimethylpentane	$y = 0.9696x + 0.3947$	0.994	0.05
n-Heptane	$y = 0.9678x + 0.3635$	0.994	0.05
Methylcyclohexane	$y = 0.9819x + 0.3629$	0.995	0.05
2,3,4-trimethylpentane	$y = 0.9691x + 0.3994$	0.994	0.04
Toluene	$y = 0.9696x + 0.3397$	0.995	0.05
2-methylheptane	$y = 0.9603x + 0.4835$	0.990	0.04
3-methylheptane	$y = 0.9625x + 0.4550$	0.991	0.04
n-Octane	$y = 0.9524x + 0.5082$	0.989	0.04
Ethylbenzene	$y = 0.9629x + 0.4253$	0.992	0.04
m, p- Xylenes	$y = 0.9541x + 0.5844$	0.986	0.03
Styrene	$y = 0.9524x + 0.4132$	0.991	0.04
o-Xylene	$y = 0.9515x + 0.4926$	0.989	0.04
n-Nonane	$y = 0.9878x + 0.1635$	0.998	0.04
i-Propylbenzene	$y = 0.9418x + 0.5162$	0.986	0.04
n-Propylbenzene	$y = 0.9426x + 0.5468$	0.986	0.04
m-Ethyltoluene	$y = 0.9532x + 0.4838$	0.989	0.04
p-Ethyltoluene	$y = 0.9554x + 0.3953$	0.992	0.04
1,3,5-Trimethylbenzene	$y = 0.951x + 0.4724$	0.989	0.04
o-Ethyltoluene	$y = 0.9784x + 0.0956$	0.999	0.04
1,2,4-trimethylbenzene	$y = 0.9563x + 0.4509$	0.991	0.03
n-Decane	$y = 0.9651x + 0.3068$	0.995	0.04
1,2,3-trimethylbenzene	$y = 0.9537x + 0.3191$	0.993	0.04
m-Diethylbenzene	$y = 0.9541x + 0.4494$	0.991	0.04
p-Diethylbenzene	$y = 0.9607x + 0.3788$	0.993	0.04
n-Undecane	$y = 0.9519x + 0.3329$	0.992	0.04
n-Dodecane	$y = 0.9890x + 0.2711$	0.993	0.05

In Lines 176-178: Please provide the input details for the machine learning simulations. For example, which set of data was used to train the model, and which set of data was used for validation? In addition, in Line 177, please

clarify the R and P values. Is it the Pearson correlation coefficient or coefficients of determination and is the p-value calculated from one- or two-tailed t-test?

Reply: Thanks for the question. In our study, we didn't use machine learning to do prediction. We took advantage of Stepwise Regression Analysis to explain how meteorological factors impact O_3 concentrations. In detail, we constructed a multivariate linear regression equation to model O_3 concentration. Meteorological parameters were obtained from the fifth generation of the European Centre for Medium-Range Weather Forecasts atmospheric reanalysis (ERA5). The selected parameters included 10m u-component of wind (U10), 10m v-component of wind (V10), vertical wind (w), boundary layer height (BLH), 2m temperature (T2) and surface solar radiation (SSR). Additionally, we also incorporated previous night accumulative air pollutants, such as O_3 (ACCO3) and NO_2 (ACCNO2), as input parameters to investigate the impact of pollutants being overnight accumulated on O_3 levels. The machine learning-simulated O_3 concentrations were then validated against observations, revealing a robust correlation (Pearson correlation coefficient (R) > 0.91, p-Value (from two-tailed t-test) < 0.01) between them (Fig S1).

In Line 191: JNO2 were measured during the sampling period, while the authors did not introduce the instrument for JNO2 measurements. Please provide this information in Section 2.1.

Reply: Thanks for the careful review. We have added "The photolysis rate of NO_2 (J_{NO2} value) were measured by Ultra-fast CCD-Detector Spectrometer (UF-CCD, MetCon, Germany)" in Section 2.1

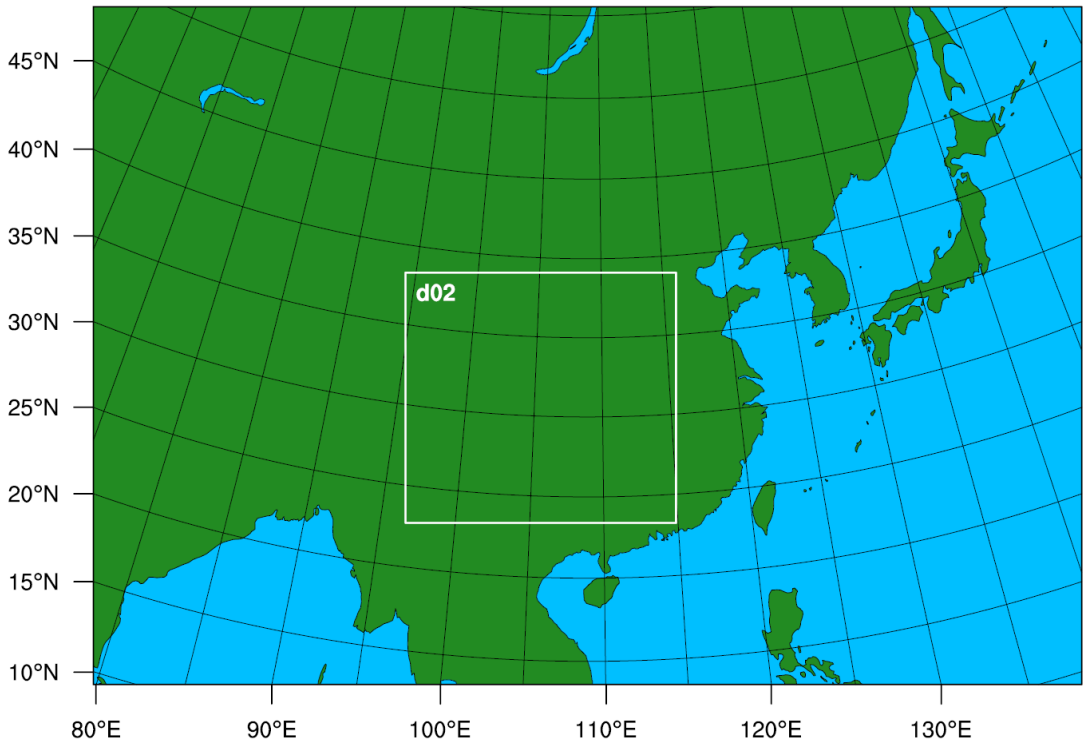
In Lines 216-220: Please explain how the backward trajectory of 3000 particulates was.

Reply: In this study, the LPDM simulation was conducted with the aim to understand the potential source region impacting Chengdu and Chonging. We released 3000 particulates as tracers over the site to investigate their 72-hour backward movement. 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. The introduction of the LPDM has been presented in Section 2.4.

In Section 2.5: My suggestion is to add a figure to illustrate the domain coverage and provide statistical or graphical evaluations of the modeled meteorological fields against observations. In addition, though the simulated O3 concentrations have good statistical agreements with those observed as shown in Fig S3, there were still some biases in Chengdu, Nanchong, and Deyang. Some discussions on the discrepancies are needed.

Reply: Thanks for the suggestion. We have done the following revisions,

(1) We have added a figure to illustrate the domain coverage in the supplementary file. Please see Fig S2.



Figs S2 Domain coverage of the WRF-CMAQ model. The outer box shows the domain of d01 and the inner box shows the domain of d02.

(2) Evaluations of meteorological simulations including temperature, relative humidity and winds were summarized in Table S4. Generally, these meteorological parameters matched well with the observations, with high correlation coefficient and low bias. It was notable that the wind speed was a little overestimated, which

was a common issue for weather numerical simulations, especially for a grid resolution of 12×12km.

Table S4 Statistical validation of WRF simulated meteorological parameters.

	MB	RMSE	R
Temperature (° C)	-0.6	2.1	0.91
Relative humidity (%)	-4.5	8.6	0.86
Wind speed (m/s)	1.6	1.8	0.45

(3) It is important to emphasize that we have included the results of the CMAQ model spin-up in our presentation. The initial five days were dedicated to model pre-warming, and as a result, there is a significant disparity between the simulated ozone and observations during this initial period. Please see our revisions, "After a spin-up of 5 days, the WRF-CMAQ model was performed to simulate O_3 concentrations in the SCB."

Based on the validation, it could be found out that we captured the changing trends of basin ozone and successfully replicated the simulation of summer ozone pollution as evidenced by the high value of IOA (0.78~0.85). We admit that there was difference between the simulations and observations in some details, this was mainly attributed to the highly complex topography of the Sichuan Basin, characterized by high elevation differences and deep basin topography, posing significant challenges to our numerical simulations. One method to improve

simulation results is to increase the model's resolution. Constrained by the spatial resolution of the MEIC inventory (0.25° × 0.25°), we adopted a grid resolution of 12 km × 12 km in this study. Therefore, we also call for the development of higher-resolution emission inventories in the future to enhance the performance of air quality numerical simulations.

In Lines 251-256: The authors could further introduce how the DDM method was more refined than the BFM method.

Reply: Thanks for the question. We have incorporated the following introduction in the manuscript, "In this study, we introduced the CMAQ-DDM (Decoupled Direct Method) module to investigate the non-linear relationship between O_3 and its precursors. Unlike the traditional brute force method (BFM) that involves cutting or eliminating emissions from source regions (or sectors), which is not only computationally intensive but also prone to uncertainties (due to the intricate non-linear nature of O_3 chemistry), the DDM method offers a more refined alternative. It enables accurate and computationally efficient calculations of the sensitivity coefficients required for evaluating the impact of parameter variations on output chemical concentrations (Napelenok et al., 2008). Furthermore, the DDM method has been reported to exhibit more accurate calculations when addressing uncertainties arising from the

nonlinear relationship between secondary pollutants and their emissions, in comparison to the BFM (Itahashi et al., 2015)."

In Fig 3: Please introduce each factor in the figure caption.

Reply: Thanks for the suggestion. We have added the factor in the figure caption, "Temp, SSR, BLH, U10, V10, W, $ACCO_3$ and $ACCNO_2$ stands for temperature, surface solar radiation, boundary layer height, 10 m u-component of wind, 10 m u-component of wind, vertical wind, previous night accumulative O_3 and previous night accumulative NO_2, respectively"

In Lines 452-454: The contributions of heatwave events to isoprene emissions were quantified in two cities. Is it based on MEGAN model simulation? Please elaborate on the calculation process.

Reply: Yes, we adopted MEGAN model to calculate isoprene emission. As shown in Section 2.5, we have presented the introduction of the model, "Besides, natural emissions were calculated using MEGAN model (version 2.1) driven by the WRF simulated meteorology. The static input vegetation-related data of MEGAN were updated by using the 2020-based the plant function type (PFT) and leaf area index (LAI) retrieved from the MODIS (Moderate-Resolution Imaging Spectroradiometer) products". Here, we used two sets of meteorological fields to drive the MEGAN model. One set corresponds to the meteorological fields simulated by WRF

for the summer of 2021, while the other set corresponds to the meteorological fields simulated by WRF for the summer of 2022. Among these, the BVOC emissions obtained by driving the MEGAN model with the meteorological fields from the summer of 2021 are considered as ISOP emission by base meteorology (BaseMETE). The difference in BVOC emissions obtained by driving the MEGAN model with the meteorological fields from the summer of 2022, compared to Base METE, is considered as ISOP emission induced by heatwave (ByHeatwave). We have added the illustration in the manuscript.