Response letter for EGUSPHERE-2024-3180

Dear Editor and Reviewer:

We sincerely appreciate your help with our manuscript entitled "What makes the less urbanized city a deeper ozone trap: implications from a case study in the Sichuan Basin, southwest China" (EGUSPHERE-2024-3180) submitted to *Atmospheric Chemistry and Physics*. Your review efforts and valuable comments have been very helpful in improving the quality of the manuscript. We have carefully studied all the comments and made revisions according to the suggestions. We hope that our revisions could address your concerns on the manuscript adequately. The revised portions are marked in **red** or **blue** in the revised manuscript, and the responses to the reviewers in this document are in **blue**. In this response document, the line numbers marked to the comments (in black) indicate the lines in the previous clean version of revised manuscript, while the line numbers in **blue** text indicate the lines in the current revised manuscript (marked changes). The corrections and responses are summarized as follows:

■ Response to Reviewer #1

General Comments

Wang and coauthors present on urban-rural gradients of O_3 and NO_x extending from two cities within the Sichuan Basin. Although the authors do not introduce entirely novel concepts, the clarity of the analysis and the unique geographical context of the study make the manuscript a useful contribution to the field. While the potential causes for the observed gradient are clearly outlined, a more thorough discussion on NO_x-limited vs. VOC-limited chemistry would greatly enhance the depth of the analysis and could help explain seasonal differences in the observed trapping patterns. Specifically, expanding the focus beyond O_3 titration and loss in the city center to explore how the O_3 production sensitivity regime varies across the urban-rural gradient would add significant value. A simple and brief way to approach this could be by examining how the formaldehyde to NO_2 ratio changes from VOC-limited

to NO_x-limited conditions across the gradient for the two cities seasonally. With this addition, along with addressing the specific comments below, I believe the manuscript would be suitable for publication.

Author's response: We sincerely appreciate your review efforts. Following your guidance, we have analyzed the ratio changes of formaldehyde to NO_2 from VOC-limited to NO_x-limited conditions across the gradient for the two cities seasonally, some new findings to explain the ozone trap discrepancy were obtained. Shown as β (ratio of NO_2 to formaldehyde) over the basin (**Figure R1**), the concentration of NO_2 is lower than formaldehyde in all areas during summer. But in winter, the two megacities exhibited concentration centers where NO_2 was significantly higher than formaldehyde.

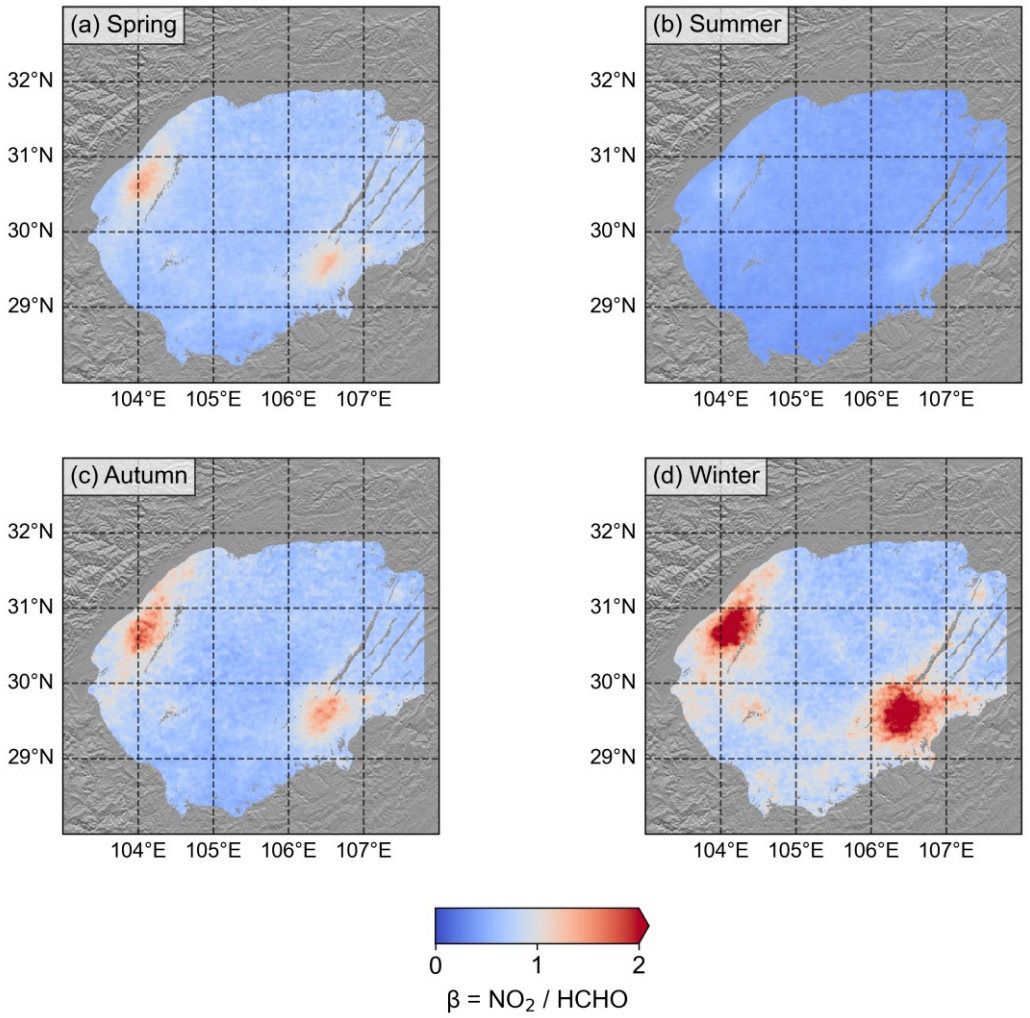

Figure R1 Spatial patterns for the number concentration ratio of NO_2 to formaldehyde over seasons during 2019-2023.

Then, we calculated β across different ISA (impervious surface area) levels (**Figure R2**). With increasing ISA, the summer β steadily rises within the range of 0.5~0.6, while the winter values reach a level of 1.2~1.8. Combined with the spatial pattern maps mentioned above, it can be clearly observed that the spatial distribution characteristics of β are primarily determined by NO_2.

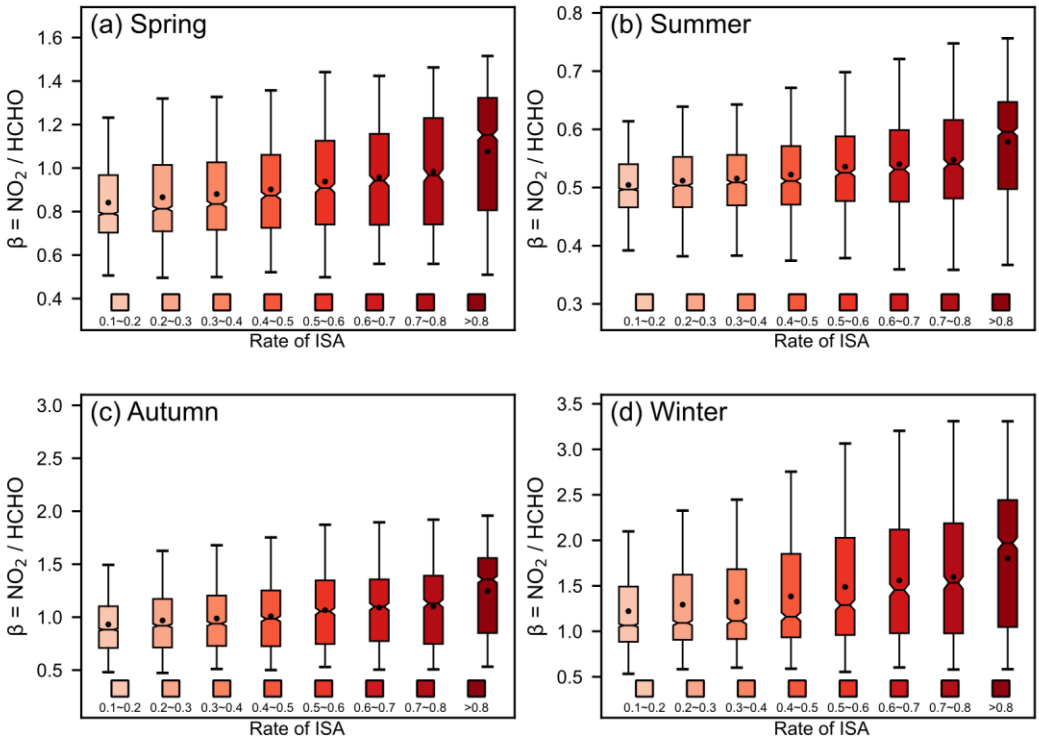

Figure R2 Response of β to rate of ISA over seasons during 2019-2023. The solid lines in the mid of the boxes are medians, the notches are the 95% confidence interval of the medians, the black dots are mean values, and the whiskers are interquartile ranges.

Further, we examined the urban-rural gradients of β across the two cities. It is found that although the gradient of NO_2's urban-rural decay curve in Chongqing is smaller than that in Chengdu, the decay curves of β are nearly identical. Notably in winter, the decay level at 100 km from the urban center even exceeds that of Chengdu (**Figure R3**). Quantitatively, during winter, the core area level and urban-rural slope of NO_2 are 57.8 μg m^{-3} and -5.34% in Chengdu, while 49.6 μg m^{-3} and -3.17% in Chongqing, respectively (**Table R1**). When we examine the β instead of solely examine the pattern of NO_2, it is found that while Chengdu demonstrates a steeper urban-rural decay rate in NO_2 concentration compared to Chongqing, the β reveals an inverse pattern—both core area levels and decay rates are higher in Chongqing. Therefore, under the condition of

ozone gradient 6.49% (Chongqing) versus 1.88% (Chengdu), although β does not play a decisive role, the spatial behavior of β likely contributes a certain portion to Chongqing's more pronounced ozone sink effect relative to Chengdu.

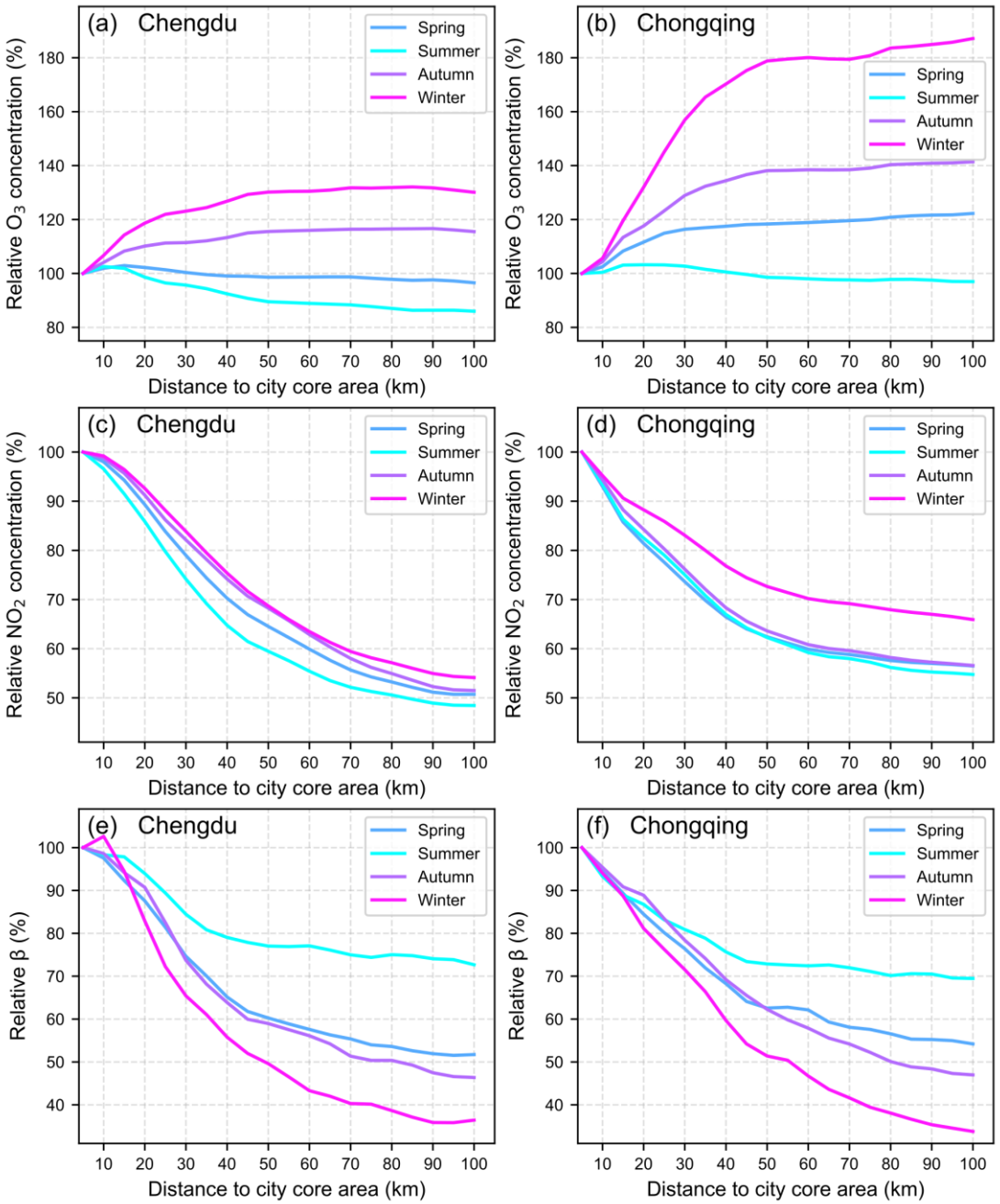

Figure R3 Relative O_3, NO_2, and β levels along with the core area distance in Chengdu (a, c, e) and Chongqing (b, d, f) over seasons. The average value within a 5-km radius centered to the city core area is used as the reference value. The gradients are referred within 5~100 km.

Table R1 Averaged concentrations within 5-km radius centered to the core area and the urban-rural gradients (to 100 km away) of relative O_3 and NO_2 levels, and NO_2/HCHO ratio.

City	Pollutant	Season							
		Spring		Summer		Autumn		Winter	
		core	slope	core	slope	core	slope	core	slope
Chengdu	O_3	110.1	-0.50	127.8	-1.67	62.3	1.02	47.9	1.88
	NO_2	55.7	-5.26	44.9	-5.07	51.0	-5.49	57.8	-5.34
	NO_2/HCHO	1.38	-4.78	0.67	-2.23	1.65	-5.34	2.43	-6.22
Chongqing	O_3	78.1	1.03	117.3	-0.56	48.0	2.80	27.5	6.49
	NO_2	49.3	-3.46	40.1	-3.91	47.8	-3.88	49.62	-3.17
	NO_2/HCHO	1.28	-4.15	0.65	-2.20	1.42	-5.66	2.53	-6.77

Note: Values on the left side are core area concentrations of O_3 and NO_2 (μg m^{-3}), while on the right side are concentration slopes (% (10 km)$^{-1}$), representing the variability of O_3, NO_2 concentrations for every incremental 10 km radius distance centered to the city's core area. The NO_2/HCHO indicates a ratio of between NO_2 and HCHO during 2019-2023 from Sentinel-5P, their core area concentration levels and slopes are calculated in the same way as above.

Specific Comments

Line 45: This could be more quantitative. What is the projected increase in ozone and what are the climate and emission changes?

Author's response: Revision done. Now the sentence is in Line XXX: Climate warming and reduced NO_x emission will exacerbate ozone pollution, until 2050, summer ozone levels over southwestern China are projected to increase by 10~15 ppbv.

Lines 50 – 55: This is also too qualitative. There should be numbers for discrepancies, increases, etc.

Author's response: Revision done. Now the sentences are: Similar low to high discrepancies of O_3 levels from urban to rural are also found in U.S.A, Spain, U.K, and Turkey. Specifically, O_3 observations from urban sites showed approximately 20 ppbv lower than rural sites in the New York City (Stasiuk and Coffey, 1974). In Málaga city of Spain, ozone concentrations at the urban station vary from 184 to 5 μg m^{-3} and the values at the rural site vary from 189 to 11 μg m^{-3} (Dueñas et al., 2004). The highest daily urban and rural ozone concentrations were 199 μg m^{-3} in London and 222 μg m^{-3} in Yarner Wood in the southwest region of England (Atkinson Richard et al., 2012). The O_3 levels in semi-rural and rural sites in Istanbul of Turkey during observation period

are 64 ppbv at the urban, 80 ppbv at the semi-rural and 100v ppb at the rural site (Im et al., 2013). O_3 observations from Madrid of Spain showed averaged hourly concentrations range around 30~80 μg m^{-3} (urban sites) and 40~100 μg m^{-3} (rural sites) (Betancourt-Odio et al., 2021).

Line 67: There should be a new paragraph that sets up the manuscript. The transition to introducing the study is not clear. In particular, the statement that starts with "However, by presenting…" should be rewritten to introduce your study.

Author's response: Revision done. Now the newly started paragraph is: However, our study presented the surface ozone spatial behavior based on a 7-year-long climatology, indicating the trap pattern of surface ozone is a regular situation under certain seasonality. Then, we presented a quantified spatial analysis for the urban-rural gradients, which has not been addressed in previous studies. We utilize a 1-km-resolution pollutants dataset (**section 2.3**) to characterize the long-term averaged spatial behavior, as well as illustrated the relationship between pollutant concentration and urbanization level using satellite-based high-resolution land surface cover data (**section 2.2**). Our analysis of the urban-rural concentration discrepancy in the Sichuan Basin revealed the phenomenon of surface ozone trapping in the highly urbanized city core area. These results can enhance our understanding of the source-sink mechanism and key factors affecting surface ozone level.

Figure 4/Table 1: How many CAQRA sites are within your study region? The plots in figure 4 seem like smooth bilinear interpolations which could be biasing your slopes. Can you either report some statistics of distance between sites (e.g., median, mean, max) or a validation of measurements from your sites within your domain rather than the whole network?

Author's response: The CAQRA dataset collected most of CNEMC observations over China, the number of observation sites was approximately 510 in 2013 and increased to 1436 in 2015 (**Figure R4**). In our study region, this number ranges among 20~100, the urban sites are relatively denser, spaced approximately 5~20 km apart, while suburban sites are sparser, with distances exceeding 50 km. The original spatial

resolution of CAQRA is 15 km. To conduct our spatial pattern analysis, we interpolated it into 1 km horizontal resolution, left certain biases to the slopes.

However, we utilized new datasets to mitigate this omission. In 1 February 2025, a dataset named O_3 concentration dataset for mainland China (ChinaHighO_3) was released (Yang et al., 2025). This dataset used hybrid numerical dynamic modeling and machine learning works, produced 1 km horizontal resolution gridded data over China. Moreover, the ChinaHighO_3 belongs to a dataset series named CHAP (China High Air Pollutant) (Wei et al., 2023), all produced using similar methods as high-resolution air pollutant datasets. Most importantly, as we applied new datasets to our study, the results are highly consistent with previous findings (based on interpolated CAQRA) in terms of spatial patterns, still supporting the conclusion of a dipole-like ozone trapping pattern (**Figure R5, R6**).

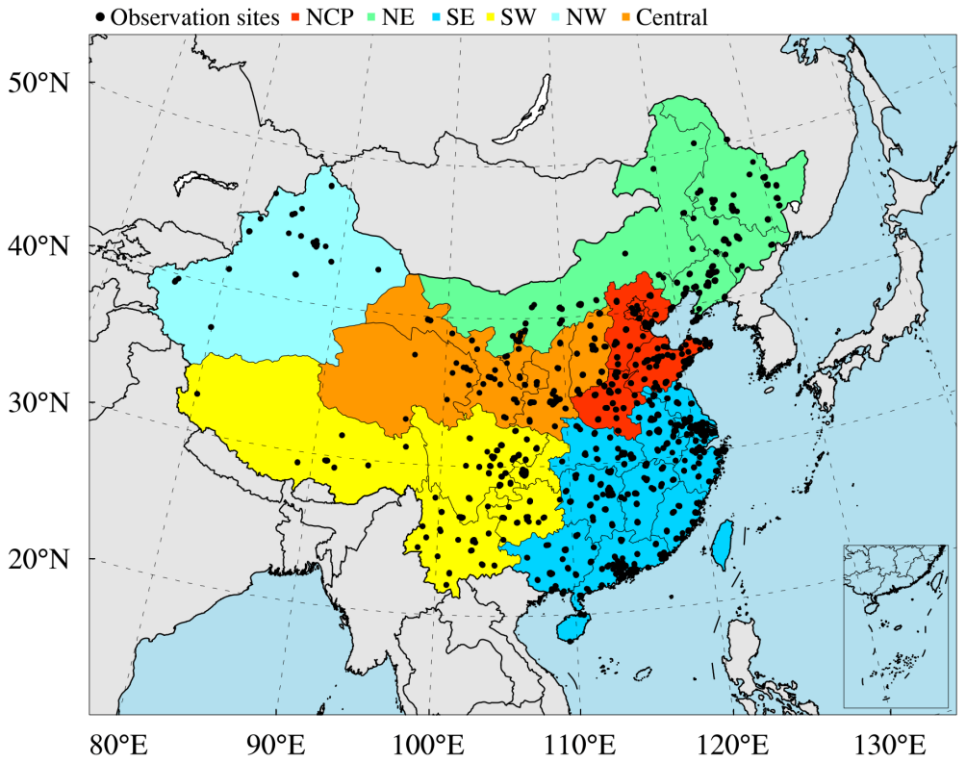

Figure R4 The distribution of the observation sites of the China National Environmental Monitoring Centre (CNEMC). The different colors denote the different regions in China, namely, the North China Plain (NCP), northeast China (NE), southwest China (SW), southeast China (SE), northwest China (NW), and central China. (Kong et al., 2021)

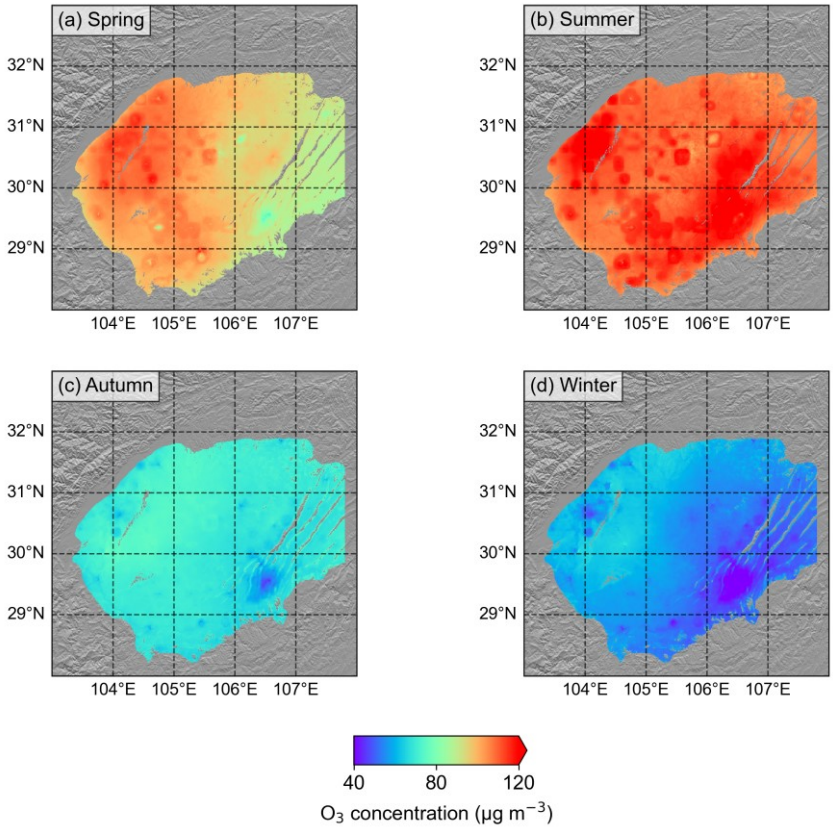

Figure R5 Spatial patterns for ozone (O_3) concentrations over seasons during 2013-2019 from ChinaHighO_3.

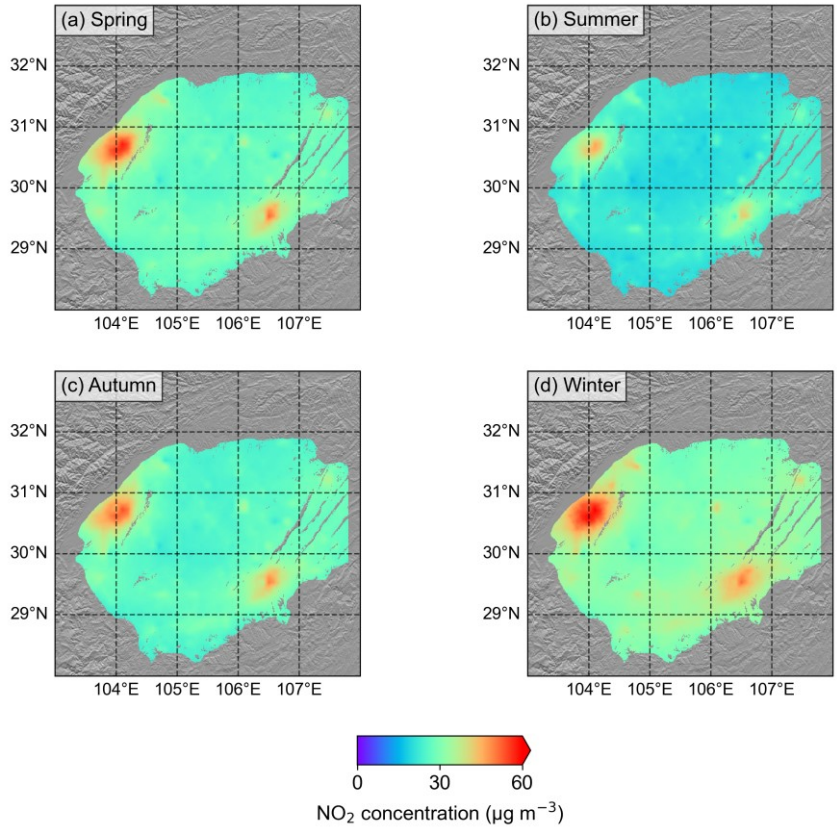

Figure R6 Spatial patterns for nitrogen dioxide (NO_2) concentrations over seasons during 2013-2019 from China High Air Pollutant (CHAP) dataset.

References:

Wei Jing, Li Zhanqing, Wang Jun, Li Can, Gupta Pawan, Cribb Maureen. Ground-level gaseous pollutants (NO_2, SO_2, and CO) in China: daily seamless mapping and spatiotemporal variations. *Atmospheric Chemistry and Physics*, **2023**, 23(2): 1511-1532. https://doi.org/10.5194/acp-23-1511-2023.

Yang Zeyu, Li Zhanqing, Cheng Fan, Lv Qiancheng, Li Ke, Zhang Tao, Zhou Yuyu, Zhao Bin, Xue Wenhao, Wei Jing. Two-decade surface ozone (O_3) pollution in China: Enhanced fine-scale estimations and environmental health implications. *Remote Sensing of Environment*, **2025**, 317: 114459. https://doi.org/https://doi.org/10.1016/j.rse.2024.114459.

Line 183: While you do present figures and some ranges, there should be numbers backing your statement that the concentration range became wider in higher ISA fraction bins either by a normalized IQR or select ranges for ISA bins.

Author's response: Revision done. These ranges are the mean values among different ISA levels in a certain season. Now we regenerated the data, and made a clearer expression: These results indicate that in cold seasons (autumn and winter), only a certain part of the highly urbanized areas experienced a significantly lower O_3 level. Ranging among all ISA bins, the mean values of O_3 level are more than twice as high in summer (115.8~ 121.1 μg m^{-3}) as in winter (48.8~54.3 μg m^{-3}). In contrast, the NO_2 levels are higher in winter (38.1~46.6 μg m^{-3}) than in summer (26.5~33.8 μg m^{-3}).

Line 222-223: How far away from the city core area are the slopes calculated for? In Figure 8 there are two distinct slopes for relative concentration and distance from city center.

Author's response: The gradients are referred within 5~100 km. In revision, we added clear description about obtaining the gradient to all related figures and tables.

Line 229-231: The fact that Chongqing has a deeper O_3 trap at lower NO2 levels compared to Chengdu makes me want to see the differences in production sensitivity regimes as per my general comment.

Author's response: Revision down. Given the above response to your general comment, we have added these analyzes in the revised manuscript.

Line 245, Figure A5: What about formaldehyde columns in the summertime? Do they increase and would that help explain O_3 production and a decrease in the urban-rural slope in the summertime?

Author's response: The column density of formaldehyde reaches its peak in summer (**Figure R7**). Comparing to wintertime, the formaldehyde density is 29.4 10^{-4} g m^{-2} higher in the core area of Chengdu during summer, and 40.5 10^{-4} g m^{-2} in Chongqing (**Figure R8**). It is worth noting that in Chongqing during winter, formaldehyde showed its only positive slope (**Figure R8b**), indicating a low center in Chongqing's city core area, while in Chengdu or summertime it is always a high center. This could be a firm contributor to the O_3 trap pattern in Chongqing.

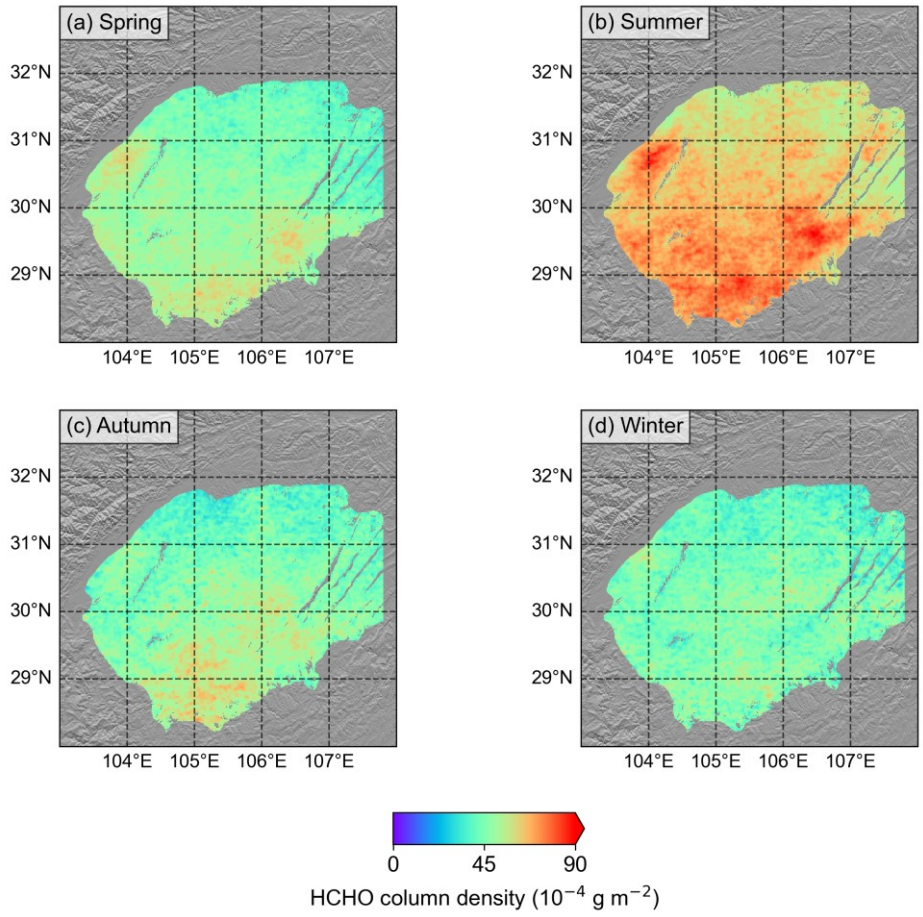

Figure R7 Spatial patterns for formaldehyde (HCHO) column density over seasons from Sentinel-5P products.

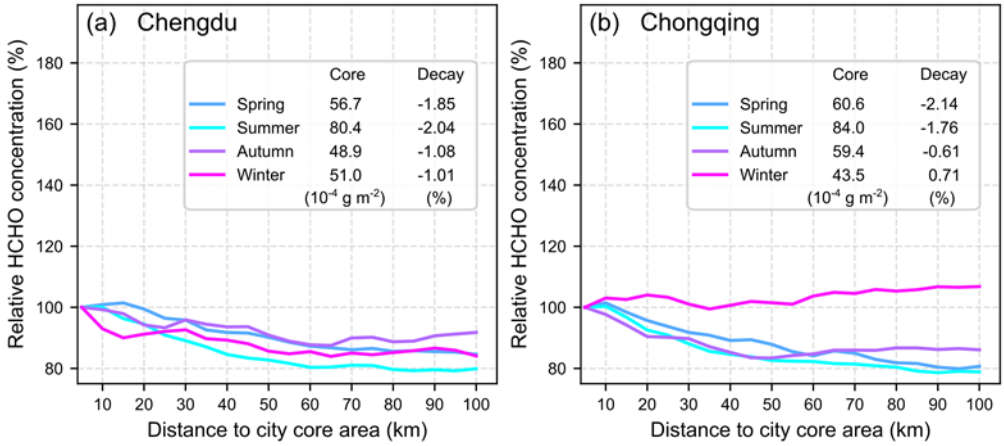

Figure R8 Relative HCHO levels along with the core area distance in Chengdu (a) and Chongqing (b) over seasons. The average value within a 5-km radius centered to the city core area is used as the reference value. The gradients are referred within 5~100 km.

Line 270-271: It is unclear how you got to this conclusion that the meteorological conditions align more closely than chemical conditions based on the preceding paragraph. Was this determined from shorter daylight hours and nighttime wind speeds? While there may not be a difference across the gradient and between cities in the same season, shouldn't seasonal surface/air temperature also be a cause for higher O_3 since it increases emissions of both anthropogenic and biogenic VOCs in a VOC-limited region?

Author's response: Revision done. Based on the new analysis of formaldehyde and its ratio to NO_2, we proposed a new conclusion here: Chongqing's more pronounced ozone depletion phenomenon stems from three contributing factors. Chemically, the region exhibits a more severe VOC-limited regime; meteorologically, weaker sunlight slows down photochemical reactions, while lower wind speeds hinder timely replenishment of ozone in the urban core area, exacerbating spatial ozone gradients.

I am also unclear on the windspeed relationship since only nighttime windspeeds are presented. From what I am reading, Chengdu has a higher nighttime windspeed and thus more dispersed and lower NO2 and higher O_3. Wouldn't dilution also affect O_3 to the same extent? Why is only nighttime presented and what about daytime dilution? Line 278-280: It is not clear why PM would be a cause for O_3 changes rather than just correlated. When the boundary layer is low in the winter PM and

NO_x concentrations may be higher due to minimized vertical dilution, with NO_x titration removing the O_3, not PM. Can you explain briefly why PM could "modulate the balance of NO titration and O_3 production"? Is it through uptake of HNO_3 and H_2O_2?

Author's response: The windspeed patterns are shown both for daytime and nighttime in **Figure 11** of original manuscript (**Figure R9** in response letter), daytime windspeed showed little difference between the two cities, their main difference appeared at nighttime. This wind dilution also affects O_3 to the same extent indeed, thus the higher windspeed in Chengdu results in a smaller urban-rural ozone gradient precisely.

PM can modulate the balance between NO titration and O_3 production through several mechanisms, primarily involving interactions with key chemical species like HNO_3 and H_2O_2. First is the uptake of HNO_3, PM (especially fine particles like $PM_{2.5}$) can adsorb HNO_3, a product of NO_2 oxidation ($NO_2 + OH \rightarrow HNO_3$). This uptake reduces the availability of HNO_3 for photolysis or re-release as NO_x, indirectly altering the NO_x cycle. Then is the scavenging of H_2O_2, H_2O_2 is a critical oxidant that converts SO_2 to sulfate and NO_x to nitrate. PM surfaces can catalytically decompose H_2O_2, reducing its atmospheric concentration. Lower H_2O_2 levels slow the oxidation of NO_x to HNO_3, prolonging NO_x lifetime and enhancing O_3 production via the photochemical cycle ($NO_2 + h\nu \rightarrow NO + O_2$). Additionally, PM can alter the fate of radicals (e.g., OH, HO_2) by providing surfaces for heterogeneous reactions. For example, HO_2 uptake by PM reduces its conversion to OH, slowing O_3 production pathways. In polluted environments, PM may also promote secondary organic aerosol (SOA) formation, which competes with O_3 for VOC precursors.

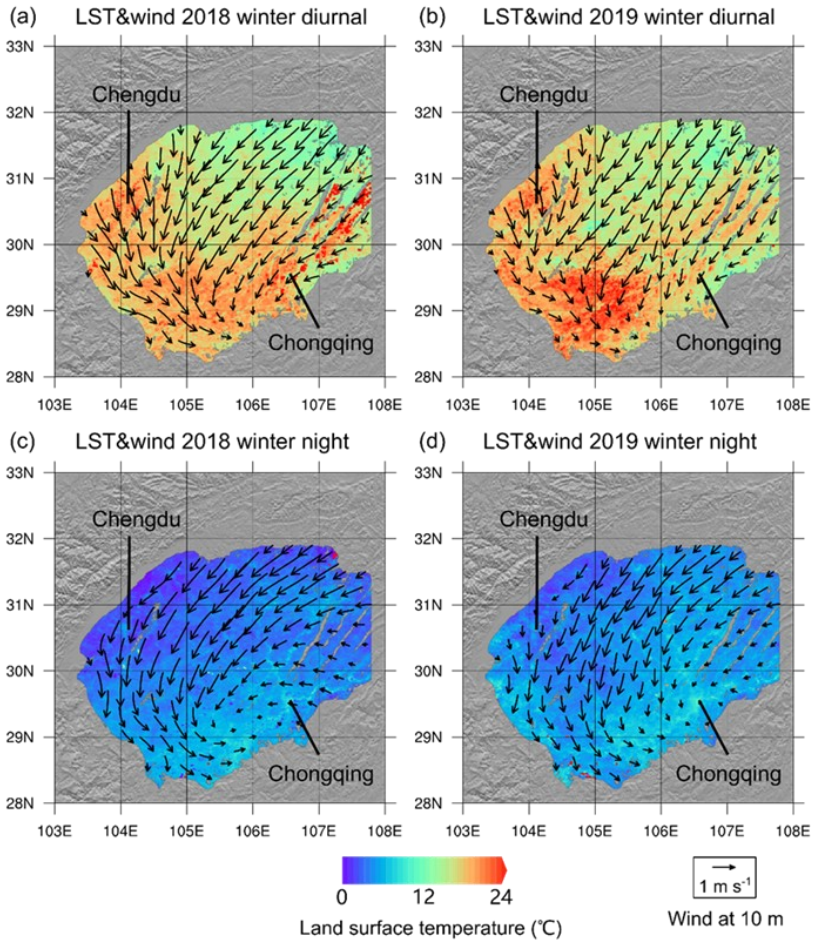

Figure R9 Land Surface temperature and 10 m wind from MODIS Aqua and ERA5-Land.

Lines 325-326: You state here that winds are lower during the cold season, but only nighttime data is presented. A more thorough and quantitative discussion of meteorological conditions in the paragraph of lines 270-271 would be helpful for supporting the claim that meteorology rather than chemistry drives this seasonal pattern.

Author's response: Revision done. As we have stated in the above response: The windspeed patterns are shown both for daytime and nighttime in **Figure 11** of original manuscript (**Figure R9** in response letter), daytime windspeed showed little difference between the two cities, their main difference appeared at nighttime. This wind dilution also affects O_3 to the same extent indeed, thus the higher windspeed in Chengdu results in a smaller urban-rural ozone gradient precisely.

Technical Corrections

Line 34: change "condition" to "conditions"

Author's response: Revision done.

Line 38: In general, when referring to compounds broadly, an article is not needed. For example "Conversely, the NO…" should change to "Conversely, NO…". This should be applied to the rest of the manuscript.

Author's response: Revision done.

Line 41: Citation error for Anenberg et al. Remove "Susan".

Author's response: Revision done.

Line 185: There is a stray T at the start of a sentence.

Author's response: Revision done.

Line 196: Figures should be presented in order. So, if presenting the contents of Figure 9 at this point you should briefly describe it here and label it as Figure 7.

Author's response: Revision done. As we rearranged our analyzes and figures, now all figures are in a rational order.

Line 290: Change to "VOC-limited".

Author's response: Revision done.

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