Dear Editor,

We have carefully considered all comments and suggestions. Listed below are our point-by-point responses to all comments and suggestions of two referees (Reviewer's points in black, our responses in blue).

In response to a key comment of Referee #1, we decided to elaborate in the revised manuscript on the saturation at high-concentration sites by adding a new section "3.3.4 Saturation at high-concentration sites" plus a new figure (Figure 16), to which Shanshan Ouyang had contributed significantly. We hereby inform and explain that to you.

Referee #1

The revision has partly addressed my concerns. The clarity of sections 3.1 and 3.2 has been largely improved. However, Section 3.3 is still not convincing and does not show sufficient novelty to meet ACP standard. It may require another round of substantial revision. My comments are to the revision-tracked version.

Response:

Instead of disputing the level of novelty of this study, we would like to point out that this study is the first (i.e., original) to suggest that "changes in meteorological conditions" rather than "changes in emissions" are the cause of of positive ozone trends in the three megacity clusters in eastern China during 2015–2020. We believe that the level of originality is a critical merit for publishing a paper. Moreover, the prevailing view on the cause is "changing emissions", this study is trying to change that view, and we believe the balance of evidence is in our favor.

Regarding Section 3.3, we understood your concern and decided to elaborate on the saturation at high-concentration sites in a new section "3.3.4 Saturation at high-concentration sites" plus a new figure (Figure 16). Please see our response on your comment "Line 294-305: Again, why this only causes ozone increase in low-ozone sites, but not at high-ozone sites? It looks like it is an important finding from the observations but no convincing reasons are provided.”

I suggest use “variability” other than “trends” in the title and the text, because 2015-2020 are too short to derive statistically meaningful trends (only 6 data points). It also makes much more sense if the authors prefer to highlight meteorological conditions of 2017 and 2019 in their analysis.

Response:

Changing “trends” to “variability” for the short term trend a logical suggestion. We accept this suggestion, but would like to point out that all previous “emission-caused trends” papers used the term “trends” for the same short period. Moreover, we have to change most of the “trends” in the text to “increases” rather than “increased variabilities” which could have a misleading meaning.

Line 98: may rephrase to “some commonly-used methods are applied in this study.”

Response:

Thanks! Done accordingly.

Line 140-146: It is not necessary that high ozone concentrations are at urban centers, as titration would be strong at urban centers which lead to lower ozone compared to suburban regions. Please provide clear information to support this statement.

Response:

The two figures below show that, despite the titration effect, Beijing and Shanghai both have higher ozone concentrations compared to their corresponding suburban regions. So is in PRD (Figure 7, not shown).

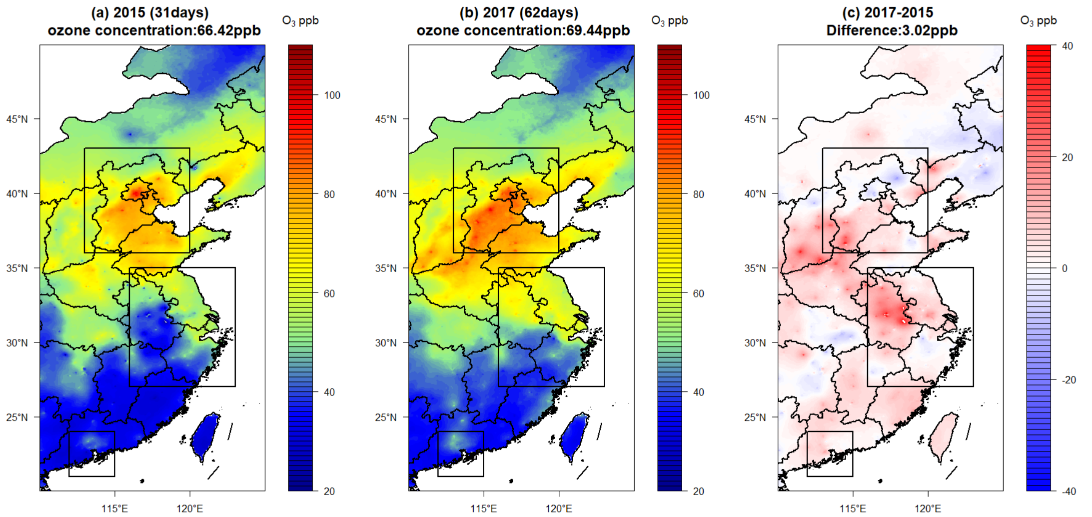

Figure 5: Spatial distribution of annual mean concentrations of maximum daily 8-hour average O_3 for O_3-exceeding days in BTH in 2015 (a), 2017 (b) and their difference (2017–2015) (c). The top, middle and bottom rectangle boxes denote BTH, YRD and PRD districts, respectively. The number inside the parenthesis behind 2015 or 2017 denotes the number of O_3-exceeding days.

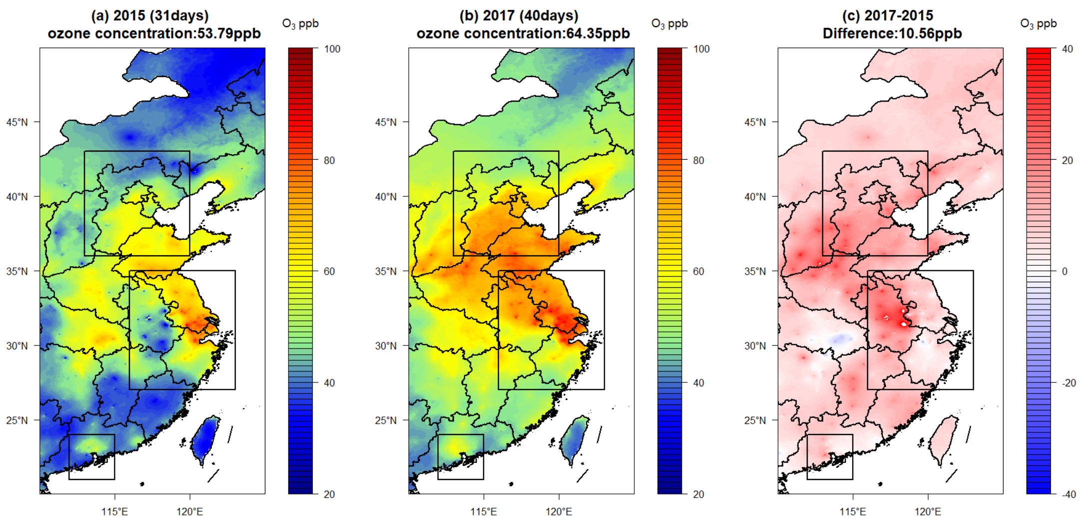

Figure 6: Spatial distribution of annual mean concentrations of maximum daily 8-hour average O_3 for O_3-exceeding days in YRD in 2015 (a), 2017 (b) and their difference (2017–2015) (c). The top, middle and bottom rectangle boxes denote BTH, YRD and PRD districts, respectively. The number inside the parenthesis behind 2015 or 2017

denotes the number of O_3-exceeding days.

Line 151: Has Figures 5 been introduced before? I suggest show raw site measurement instead of the gridded data because the later may introduced unrealistic smooths.

Response:

Figure 5 has not been introduced before. Gridded data of MDA8 O_3 in 2015–2017 were reported by Xue et al. (2020). They found that ozone site measurement data correlated well with ozone grid data. Furthermore, we found that gridded data used in Figures 5, 6 and 7 provided a better nationwide perspective of O_3 distributions and variabilities than those from site data.

Line 206-207. Many other studies have suggested this hypothesis. Suggest remove "suggested by XXX", instead just use them as references.

Response:

Agree. Done accordingly.

Line 208-209: I suggest tune down this statement. It is only a possible and partial cause.

Response:

Done as suggested.

Section 3.3: Could the title of 3.3 be something like "Causes of ozone expansion at low-concentration sites and saturation at high-concentration sites". I am still not clear whether "saturation" is a precise word to describe the "ozone remained nearly constant".

Response:

Title of 3.3 has been changed to "Causes of ozone enhancement at low-concentration sites and saturation at high-concentration sites".

Line 225-262: Suggest shorten this part. It takes too long to start the discussion of meteorology as stated by the subtitle.

Response:

Thanks! We have shortened line 225–262 by about 50% in the revised manuscript as shown below:

"Fig. 9a shows the mean daily O_3 concentrations of the first group with four or more consecutive O_3-exceeding days (labeled O_3 days≥4) in 2015, Fig. 9b shows the mean daily O_3 concentrations of the second group with less than four consecutive O_3-exceeding days (labeled O_3 days<4), and Fig. 9c is the difference between the two groups (6.10 ppb, Table 2). Figs. 9d–9f are the same as Figs. 9a–9c, respectively, but for 2017. The first group in 2017 had 28 days and mean O_3 of 74.43 ppb inside the BTH box, while the second group had 34 days and 65.32 ppb (Table 2). One of the most remarkable differences between 2017 and 2015 in Figs. 9a–9f was the large number of days with four or more consecutive O_3-exceeding days (first group) in 2017 (28 days, Fig. 9d) over that of 2015 (7 days, Fig. 9a), which alone contributed to about 62% of the difference in O_3 between 2017 and 2015 as shown in Fig. 2a (red line). Approximately 30% was contributed by the 10 days' difference (2017 vs. 2015) in the number of days with less than four consecutive O_3-exceeding days (second group). The contribution by the higher average concentration of MDA8 O_3 of the first group in 2017 is only about 8% (Table 2). These values of contributions reconfirm what is shown in Fig. 3a, i.e., the greater frequency of episodes with four or more consecutive O_3-exceeding days contributes the majority (62%) to the higher O_3 in BTH in 2017 vs. 2015, the greater intensity/concentration of O_3 during the episodes contributes only about 8%, consistent with the expansion and saturation effect discussed earlier.

The phenomena illustrated in Figs. 9a–9f also exist in YRD and PRD as well as in most other years. Figures equivalent to Figs. 9a–9c for all years in the three city clusters are provided in the Supplementary Material (Figs. S4–S6). Essential information derived from those figures is summarized in Tables 2–4.

In Figs. 10a and 10b the values of SSR and T2m of the episodes with four or more consecutive O_3-exceeding days are compared to those of O_3 episodes with less than four consecutive O_3-exceeding days, and to those of clean days (non-O_3-exceeding days). As expected, the O_3 episodes with four or more consecutive O_3-exceeding days consistently have the highest values of SSR and T2m, while the clean days have the lowest values. This is the case in nearly all years studied as shown in the Supplementary Material (Fig. S7) and is also generally true in YRD and PRD (Figs. S8 and S9)."

Line 285-294: It is still very difficult to understand what exactly explain the "saturation" at high-ozone sites. Why "This saturation effect was the result of enhanced rates of atmospheric dispersion, dry deposition and photochemical loss at high O_3 concentrations"? Please clarify with data supported.

Response:

Since this comment and the next deal with the same issue, please see our response below.

Line 294-305: Again, why this only causes ozone increase in low-ozone sites, but not at high-ozone sites? It looks like it is an important finding from the observations but no convincing reasons are provided.

Response:

We appreciate very much this insightful comment and the one above. Actually you raised the same point in the earlier round of review. The spatial expansion and saturation of high O_3 was regarded by us as an interesting empirical finding, your persistent comments make us realize that this finding may have more important and far reaching implications than previously perceived. So we decided to elaborate on the saturation at high-concentration sites by adding a new section "3.3.4 Saturation at high-concentration sites" plus a new figure (Figure 16) which are shown below.

"**3.3.4 Saturation at high-concentration sites**

Why the favorable meteorological conditions only cause O_3 increase at low O_3 stations, but not at high O_3 stations? And why the saturation O_3 level is around 100 ppb as shown in Fig. 4? These questions can be best addressed by examining Fig. 16 which depicts the time series of individual processes (where DDEP denotes dry deposition, CHEM the net photochemical production of O_3, HTRA the horizontal transport and VTRA the vertical transport) contributing to O_3 budget in PRD (averaged over 56 stations in PRD) calculated by the WRF-CMAQ model for the O_3 episode of September 24–October 1, 2019 (Ouyang et al., 2022). This episode was one of the most sever O_3 episodes since the official O_3 observation started in PRD in 2006. MDA8 O_3 exceeded the 75 ppb standard on all eight days of the episode. Hourly O_3 reached as high as 110 ppb, yet all MDA8 O_3 stayed approximately between 75 and 100 ppb. This suggests a ceiling/saturation level of approximately 100 ppb for MDA8 O_3, consistent with what was observed in Fig. 4 for PRD as well as BTH and YRD. Since this episode was one of the most sever episodes, we can assume that the 100 ppb saturation level would also be applicable to other O_3 episodes in Guangdong. More importantly, the saturation effect was also a common feature in the results of other three-dimensional models for other megacity clusters, in which MDA8 O_3 usually saturated at 100 ppb, e.g., in YRD (Li et al., 2012) and in Beijing (Zhang et al., 2023). This explains why the saturation O_3 level is around 100 ppb as shown in Fig. 4.

In regard to the first question: Why the favorable meteorological conditions only cause O_3 increase at low O_3 stations, but not at high O_3 stations? It can be understood as follows: At a low O_3 station of 65 ppb MDA8 O_3 in PRD in 2015 (Fig. 4c), Fig. 16 shows that MDA8 O_3 can readily increase to 75–100 ppb in a few hours from an early morning low ozone of about 50 ppb under favorable meteorological conditions. However, at a high O_3 station of 100 ppb MDA8 O_3 in 2015 (Fig. 4c) under the same favorable meteorological conditions, MDA8 O_3 would also reach 75–100 ppb in a few hours from an early morning low ozone of about 50 ppb (Note here we assume all stations start the day with an early morning low ozone of 50 ppb, consistent with the value in Fig. 16). In other words, the saturation levels at all stations are the same at 75–

100 ppb, independent of the ozone concentration in 2015.

In terms of contributing processes, the saturation level of 75–100 ppb is controlled primarily by photochemical loss, dry deposition and dispersion to the free troposphere. This can be clearly seen in Fig. 16, on all eight days in the mid-morning when O_3 is approaching toward its peak value, CHEM declines sharply due to photochemical loss, and HTRA, VTRA and DDEP all become greater. Near noontime O_3 starts to drop sharply."

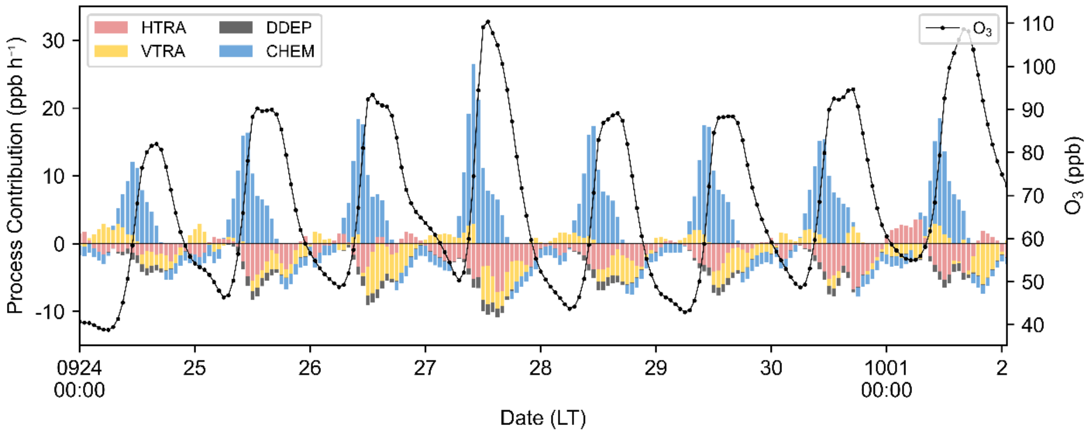

Figure 16: Time series of individual processes contributing to O_3 budget in PRD calculated by the WRF-CMAQ model for the O_3 episode of September 24–October 1, 2019. The black line (O_3) represents the averaged O_3 concentrations in the layers below 1260m. Where DDEP denotes dry deposition, CHEM denotes chemical processes, HTRA denotes the horizontal transport and VTRA denotes the vertical transport.

Finally, in the following figure the data of 2021 and 2022 have been added to Figure 4 and presented in the revised Supplementary as Figure S14. As you can see that the saturation effect remains intact (red lines stay lower than 100 ppb), while green lines stay significantly higher than those in 2015.

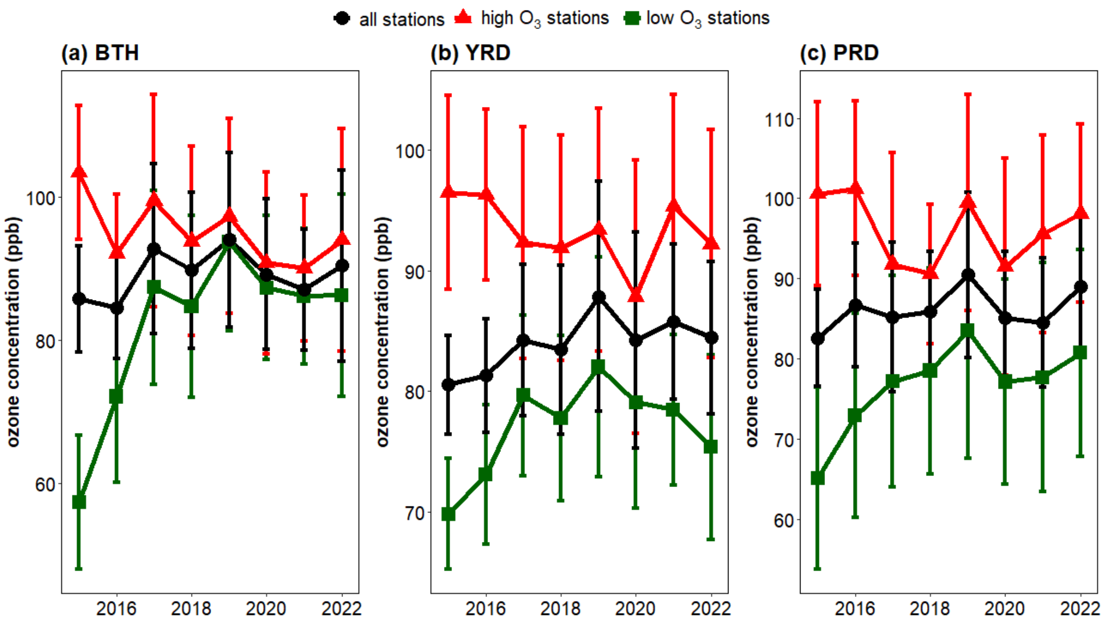

Figure S14. Annual mean concentrations of maximum daily 8-hour average O_3 during O_3-exceeding days for all stations (black), high O_3 stations (red) and low O_3 stations (green) in BTH in 2015–2022 (a), YRD (b) and PRD (c).

My judgement is that the study does not add significant novelty to the meteorological cause of high ozone in 2017 and 2019, because the impact of tropical cyclone and subtropical high is well-known. This is can be seen in Sections 3.3.2-3.3.3 that the study cites and repeats many existing research. Please highlight what's novel in this analysis. Why this happens in 2017 and 2019? Why this extends the ozone episodes? Can such weather pattern explain the observed ozone increase in low-ozone site and the saturation of high-ozone site?

Response:

Please refer to our response to your comment about the novelty at the start of this review. Please also refer to our response to your comment on the saturation of high-ozone sites around line 294–305. In addition, while "the impact of tropical cyclone and subtropical high is well-known", we deserve the credit of being the first to apply this well-known information to argue for "changes in meteorological conditions" rather than "changes in emissions" being the cause of positive ozone trends in three megacity clusters in eastern China during 2015–2020.

Figure 2. I am confused about the y-axis title of Figure 2. Ozone days has lower than 20 ppbv of MDA8 ozone? Please check carefully.

Response:

Line 99–101, we stated "The normalized annual mean O_3 concentration of the O_3-exceeding days is calculated by adding the O_3 concentration of the O_3-exceeding day each year and dividing it by the total number of days in the year. The normalized annual mean O_3 of the non-O_3-exceeding days is calculated by the same method except for the non-O_3-exceeding days."

References

Xue, T., Zheng, Y., Geng, G., Xiao, Q., Meng, X., Wang, M., Li, X., Wu, N., and Zhang, Q., Zhu, T.: Estimating spatiotemporal variation in ambient ozone exposure during 2013–2017 using a data-fusion model, Environ Sci Technol, 54, 23, 14877−14888, https://doi.org/10.1021/acs.est.0c03098, 2020.

Referee #2

I couldn't find any reference to Table R1 and Figures R1 to R3 (in Author's response document) or the corresponding information in either the main manuscript or the supplement? Please include at least some of this information in the manuscript.

Response:

Sorry for the confusion. We did put Figures R1 and R2 (where R denotes Response) in the supplementary material but rename them as Figures S1 and S3 (where S denotes Supplementary). Figure R3 was not included in the supplementary material because it was not cited in the text of the main manuscript.

Also, the following paragraph as added text in Author's response doesn't appear in Author's tracked changes. I wonder why that is?

"Hu W. et al. (2023), in collaboration with this study, conducted a statistical analysis to assess processes that contribute to high O_3 formation in PRD when TCs were present in the northwest Pacific. They investigated the impact of the distance between TCs in the northwest Pacific and PRD on the O_3 concentration in the PRD from 2006 to 2020. They found that the large numbers of consecutive O_3-exceeding days in 2017 and 2019 relative to 2015 were primarily attributable to the greater occurrence of downdrafts and stable atmospheric conditions brought about by mid-distance category TCs. This finding clearly establishes that changing frequency of mid-distance category TCs (i.e. changing meteorological conditions) is the cause of the increases in the numbers of consecutive O_3-exceeding days as well as the higher O_3 concentrations in PRD. Ongoing study by our research group further shows that the mid-distance category TCs are predominately those TCs with tracks starting around the southern Philippines and ending near Korea and/or Japan. Since TC tracks in northwestern Pacific are strongly controlled by WPSH, we conclude that both Philippines-to-Korea/Japan track TCs and corresponding distribution and intensity of WPSH contributed to the higher consecutive O_3-exceeding days in PRD from 2015 to 2020."

Response:

Please look for this paragraph around line 265–276 in the current version of the manuscript. It was around line 282–292 in the earlier version.