Dear Editor,

We appreciate the prompt reviews and would like to thank the reviewer for insightful comments and suggestions on our manuscript entitled "Observation-based Analysis of Ozone Production Sensitivity for Two Persistent Ozone Episodes in Guangdong, China". We have carefully considered all comments and suggestions. Listed below are our point-by-point responses to all comments and suggestions of this reviewer (Reviewer's points in black, our responses in blue).

Comments to the Author

In this paper by Song et al., the authors use 2 episodes in Guangdong, China and a large number of measurement sites in the vicinity to construct an observation-based method (OBM), utilizing the measurements of various pollutants from said sites alongside a box model based on the CB05 chemical mechanism, with the purpose of determining ozone production efficiency (OPE) from NOx and VOCs. They conclude that the area is under a NOx limited regime, indicating that limiting NOx emissions is the optimal strategy to reduce ozone formation in the area, contrary to previous studies.

While the paper does have its strong points – the analysis is thorough, the English used is clear and appropriate – it is not without shortcomings, many of which reviewer #1 covered. The paper merits publication based on the rigor of its analysis, but not that of the conclusions. As such I recommend the paper for publication only after the following points have been addressed and the discussion strengthened.

Response:

We appreciate the insightful comments and suggestions.

Science comments:

1. As the authors mention two episodes are not enough. In addition, they are well into

the ozone season in the fall, which could further bias the results. For example, biogenic emissions of VOCs are going to be significantly less than what they would be during the summertime, which could tip the balance of the OPE. A section should be added to discuss the potential differences between summer and fall months. The box model the authors have developed can be used, driven with meteorological variables from the observation sites during different seasons (if available), to investigate

Response:

Thank you for the very helpful comments and suggestions here and in Editorial comment 3. In response a new Fig. 1b is added which shows the average ozone concentrations of all ozone exceeding days in Guangdong in 2018 and 2019. One can see clearly that the ozone distribution during the two episodes in autumn is representative of and even slightly higher than the ozone concentrations during ozone pollution days in Guangdong in the entire two years. In fact, the monthly peak ozone concentration in Guangdong tend to occur in September and October because Guangdong is usually under heavily overcast conditions with prevailing southerly winds bringing clean moist air from the South China Sea in the summer which tends to suppress the ozone formation. We have added some discussions on this point around line 58 of the revised manuscript.

2. Based on (1), the usage of CO to VOC ratios, while a valid strategy for anthropogenic emissions completely neglects possible biogenic impacts and thus is better suited towards the urban sites much more than the rural sites. In addition to the current analysis, it would be of value that the authors also conduct the same by splitting the sites in rural and urban which would be more representative

Response:

We are conducting a follow up study by splitting the sites in rural and urban. In regard to possible biogenic impacts, we have difficulty accounting for the effect of isoprene

because it is highly variable due to its short lifetime. Nevertheless, part of the biogenic impact (up to one half) is included in our estimate of HCHO, CH_3CHO and ketones. For instance, we use observed ratio of HCHO/CO to evaluate HCHO which includes HCHO produced from biogenic VOCs. Furthermore, we have added some discussions on the uncertainty of VOCs and OVOCs around line 88 of the revised manuscript, which are copied below.

The VOCs and OVOCs derived this way can be validated by comparing with observed values in terms of the OH reactivity. Tan et al. (2019) reported that observed NOx, CO, HCHO and VOCs in PRD in autumn 2014 contributed, respectively, 14%, 10%, 5–8% and 20%, for a total of about 50% to the observed OH reactivity, which scale to 28%, 20%, 10–16% and 40%, respectively when normalized to 100%. In comparison, in our study the average NOx, CO, OVOCs and VOCs contribute 33%, 17%, 24% and 26%, respectively to the OH reactivity. There is a reasonable agreement between our results and those of Tan et al. (2019) except for OVOCs and VOCs. The disagreement on OVOCs can be easily explained by the fact that HCHO accounts for about two thirds of the OVOCs in our case. Nevertheless, the underestimate of the VOC contribution in our study remains unresolved and suggests significant uncertainty in the VOCs derived by our method.

3. I second reviewer's #1 comment about the NOx quasi steady state. This would only apply from 13:00 to 16:00. Using the average OH value for the early day is not accurate.

Response:

The following is our response to the corresponding comment of Referee #1:

We assume that the quasi-steady state of NOx in 13:00–16:00 in Fig.2 is maintained by the balance between the oxidation loss of NOx and its emission. This assumption is based on the notion that oxidation of NO_2 by OH is the predominant sink of NOx in 13:00–16:00, of which the integration over the mixed/boundary layer should be

balanced by the emission flux of NOx according to the continuous equation of NOx. Assuming the oxidation loss rate of NOx within the mixed layer is uniform with height (supported by models), we obtain that the divergence of the hourly NOx emission rate is equal to the oxidation loss rate of NOx in 13:00–16:00. Finally, we assume the hourly NOx emission rate in 13:00–16:00 can be used for 08:00–13:00, i.e. neglecting the variation in NOx emission between 08:00 and 13:00. We have added the statements above to line 137 in the revised manuscript.

4. The calculation of OPE assumes that the only real sink of NOx is the ozone formative chemistry. However, NOx is also lost to other processes and in an area like deposition and nitrate formation. The deposition is briefly mentioned towards the end, but some additional discussion and/or an estimate of the magnitude of the effect should be provided. Given the close proximity of ports in the area and therefore the likely high emissions of SO2 and subsequent sulfate formation, the additional NOx sinks could be of an important magnitude. I do realize that such an analysis would be out of the scope of the paper, and I do not require that authors conduct it, but some additional discussion on the matter is warranted, given the number of assumptions already used. On that note, particularities of Guangdong should be added to the introduction e.g., nearby ports, major highways, nearby agricultural activities etc.

Response:

We appreciate this important comment. Yes, we have neglected the heterogeneous reactions in this study. Since the effect of heterogeneous reactions is included in the observations, the neglection of heterogeneous reactions on NOx can lead to an overestimate of OH concentrations by the OBM which is a key product of this study. We have added in Section 3.5 of the revised manuscript the following paragraph on the effect of neglecting heterogeneous reactions.

Another source of uncertainty may come from the neglection of heterogeneous reactions in this study. The largest impact of neglecting heterogeneous reactions is

most likely to involve NOx between 08:00 and 13:00, during which the OH is derived. Since the effect of heterogeneous reactions is included in the observations, the neglection of any heterogeneous removal of NOx (e.g. deposition of NOx on aerosols in the humid conditions in Guangdong) can lead to an overestimate of OH concentrations by the OBM. This would have a significant impact on the outcome of this study, as OH plays a critical role in the photochemistry of NOx, VOCs and ozone. On the other hand, presence of significant natural sources of NOx such as biogenic emission and/or lightning source in 08:00–13:00 would lead to an underestimate of OH concentration.

Editorial comments:

1. The timeseries of meteorological parameters is more suited for the SI. Use the diurnal profiles instead in the manuscript, so the reader can directly go back and forth with the diurnal concentrations to clearly see the dilution effect due to the PBL.

Response:

Thanks. We have moved the timeseries of meteorological parameters to the SI in the revised manuscript.

2. While I do understand why Figure 8 was added, and it holds a lot of valuable information, it would be best to either omit it or add it to the SI. Figure 9 is more appropriate, and it would be even better if you turn it into 2D plots with variable marker sites

Response:

Thanks. We have moved Figure 8 to the SI in the revised manuscript.

3. The combined site isopleth could use some polishing; fill out the contours. Also, I very strongly recommend that you make isopleth for each of the observation site clusters from Figure 1. This also feeds into point 2 from the science comments above.

Response:

Thanks. We have improved Fig. 1 and added a new Fig. 1b to address this suggestion and those raised in point 1 of the science comments. For details please see our response to point 1 of the science comments.