Response to the Comments from Referee #1

General comments: Ozone (O_3), as a criteria air pollutant, is attracting increasing concerns in China due to the rapid rise in concentrations across the country. This paper studied the O_3 pollution in an economically boomed region of China (PRD in southern China), in terms of the meteorological impacts, local contribution and regional transport. The statistical methods were used, with interesting and meaningful results being reported. Basically, the decadal changes of O_3 in PRD were well explained, except for some aspects where further clarifications or reorganizations are needed. Though some of the findings were already known knowledge, the paper further consolidate our understandings and fully demonstrated its value in future O_3 pollution control in this region. Thus, the paper is recommended to be accepted after the following problems are addressed.

1. First, I do not quite agree with the authors' statement of the "conceptual model". Generally, a conceptual model is established based on some phenomena, and is further verified by the results. In this study, I would like to suggest the authors to replace the "conceptual model" with the "discussions" on the results, because I did not see the verification of the "model".

Response: According to Pun and Seigneur (1999), a conceptual model is a qualitative compilation of the physical and chemical processes that govern the formation of pollutants, which, to the extent possible, is supported by quantitative information. Conceptual model helps to elucidate pollutant contributions from local and non-local sources and their temporal and spatial variations, and the underlying reasons governing such variations. In this study, we use information about ozone precursor (VOCs and NO_x) emissions and their changing trends, ozone formation regimes, and the monsoonal and micro-scale synoptic conditions over different sub-regions of the Pearl River Delta to explain the spatiotemporal variations of modeling object (locally formed O_3 with meteorological adjustment). Therefore, we believe our analysis approach could be called a 'conceptual model' and would like to keep using it. Good interpretation on the modeling object (locally formed O_3 with meteorological adjustment) both under general conditions and during episodes serves as verification of the applicability of the conceptual model.

2. Second, the discussions on the O3 episodes were relatively weak and the trend analyses did not seem to be appropriate for O3 episodes, due to the limited and inconsistent number of episode days in every years. This section needs to be reorganized and some discussions should be clarified or corrected.

Response: See below responses to specific comments. We will clarify and correct some discussions in the revision.

3. Third, the discussions on O3 pollution in 2016 and 2017 look a bit weird, which should be reorganized.

Response: The logic here is that in previous sections we have examined the long-term trends of meteorological impacts, and O_3 contributions from non-local emissions and different factors of local emissions. Our statistical analysis framework also has the capability of quantitatively separating the impact of meteorology and local and non-local emissions. Actually we can do this year by year. Considering the length of the paper, we decide to show this capability in the year of 2016 and 2017, the most recent two years in the study period. We will reorganize this part in the revision to highlight our objective.

4. Lastly, it will be good if the O3 distribution, trend and the influencing factors can be discussed separately by seasons. In fact, the increases of springtime O3 in PRD in recent years were striking, in contrast to the overall unchanged O3 in summer and autumn. The paper would be more informative with the discussions on O3 pollution in different seasons and a special focus on the season when O3 is highest or increasing with the highest rates.
Response: The main point of this paper is to quantitatively examine the impacts of meteorology and precursor emissions from within and outside the PRD on the evolution of ozone during the past decade by using a statistical analysis framework combining meteorological adjustment and source apportionment and a conceptual model. Seasonal variation is indeed a very interesting issue but cannot be addressed in detail here due to the length of the paper. We will investigate it in our further study.

Specific comments:

1. Page 6, line 233-234. What were the reasons of the minor changes in O3 due to emissions during 2011 - 2015, in contrast to the significant increase before 2011? Throughout the paper, the changes in the meteorological and artificial impacts, especially the turning points of O3 variations, should be discussed.

Response: According to the PRD emission inventory developed by our research group (Figure 1 below, manuscript under preparation), increase in VOCs emission started to mitigate in 2011, while NOx emissions showed significant reduction starting from 2013. As PRD is generally in a VOC-limited ozone formation regime, reduction in the magnitude of VOCs emission increase is likely responsible for the minor changes in O_3 during 2011-2015. We will add this point in the revision.

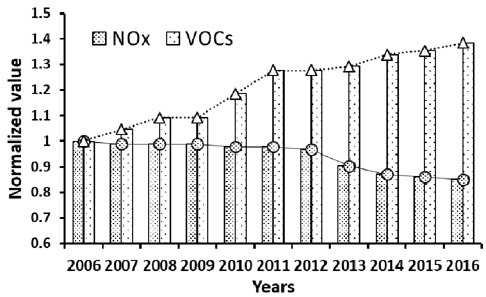

Figure 1 Emissions of NOx and VOCs in the Pearl River Delta during 2006-2016

2. Page 6, lines 236-238. The strong statement must be evidenced. This statement is actually contradictory to the later finding that "meteorological adjustment does not alter ozone concentration much" (page 9, lines 362 – 363) on episode days. Please clarify.
Response: The statement in lines 236-238 is based on Fig. 3b which clearly shows that the black ozone spikes are shortened to blue after meteorological adjustment. This indicates that meteorology plays a leading role in generating ozone episodes. It should be noted that meteorological adjustment here is against the average meteorological condition during the entire period. In comparison, the meteorological adjustment in the episodic analysis is against the average meteorological condition during episode days. Although the average meteorological condition varies greatly in different years, that during episodes does not differ much in different

years. Therefore, we conclude that "meteorological adjustment does not alter ozone concentration much" on episode days.

3. Page 6, lines 259 – 260. Please briefly explain why central and western PRD were the regions that were most sensitive to meteorological conditions in O3 pollution?

Response: Generally, area with higher pollutant emission is more sensitive to changes in meteorological condition (Seo et al., 2014). Various studies have shown that central and western PRD is the area with the most intense O_3 precursor (VOCs and NOx) emissions over the PRD (e.g. Zheng et al., 2009) therefore is more sensitive to meteorological condition. This information will be added in the revision.

4. Page 7, line 267. "…and that most local emissions are concentrated in the central PRD area". Add references to support the statement.

Response: We will revise this statement as "…and that most local emissions are concentrated in the central <u>and western</u> PRD area". Reference Zheng et al. (2009) will be added in the revision.

5. Page 7, lines 303 – 305. The reasons for picking the three sites should be given. It will be better to plot all the sites in the supplement.

Response: There is a north-south gradient in the spatial distributions of all three principal component loadings, as shown in Fig. 5a. Therefore, we select Tianhu (TH) in the north, Luhu (LH) in central, and Donghu (DH) in the south of PRD to study the long-term trend of ozone contributed by local and non-local emission sources in different areas. Ozone contributions at the other stations will be added in the supplement.

6. Page 8, lines 349 – 351. Change "strengthening" to "constraining" or "restraining". Why only VOCs should be controlled? Also, cutting VOCs emissions will not prevent the decrease of NO titration to O3. The statements should be more accurate throughout.

Response: Here we are talking about "<u>strengthening</u> local VOC emission <u>control</u>". There is a "control" at the end of the sentence, therefore we cannot change "strengthening" to "constraining". In addition, NO titration of O_3 is dependent on VOC/NO_x ratio. If the ratio is lower, NO titration of O_3 near emission sources would be higher. Therefore, controlling VOCs emission to reduce VOC/NO_x ratio would to some extent enhance NO titration so as to reduce O_3 level.

7. Page 9, lines 377 – 378. What were the causes of levelling off and decrease of non-local contributions? As commented above, the changes are worth to be discussed, which may relate to the nationwide emission controls.

Response: At this time we are not aware what the exact reason for levelling off and decrease of non-local contribution after 2014. We look at VOCs and NO_x emission inventory over non-PRD area in Guangdong Province developed by our research group (Figure 2 below, manuscript under preparation). NO_x emissions decreases and VOCs emissions increases after 2014. As most of the non-PRD area in Guangdong may in a transitional ozone formation regime in an annual average, such a slight change in NO_x and VOC emissions lead to little changes in O_3 formation and transport into the PRD. We must emphasize that the above argument is simply our speculation and further modeling study is needed to explain such a phenomenon.

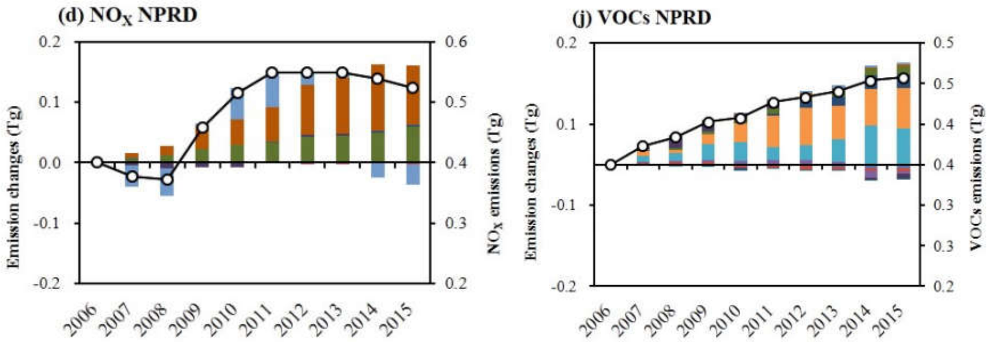

Figure 2 Emissions of NOx and VOCs in the non-Pearl River Delta of Guangdong Province during 2006-2015

8. Page 11, lines 448 – 450. It is most likely that O3 formation in the northeastern PRD became more limited by NOx, however evidences should be provided to prove the shift of O3 formation regime from VOC-limited to NOx-limited in the southwestern.

Response: There is no publication reporting the shift in O_3 formation regime in southwestern PRD, as such a shift mainly occurs in recent years. However, we may speculate such a shift during pollution episodes considering the intense biogenic VOC emissions over southwestern rural area when temperature is high and solar radiation is strong. Jin and Holloway (2015) discovered that O_3 photochemistry is NOx limited from April to October and transitional or mixed in other months using satellite observed $HCHO/NO_2$ ratio. Although there is large uncertainty by using $HCHO/NO_2$ to infer ozone formation regime, such a trend of shifting to NO_x-limited regime during ozone episodes is evidenced.

9. Page 11, lines 455 – 464. The discussions on O3 episodes need to be deepened. For example, the winds were not always from the east during O3 episodes, which in fact were from the northeast with low speeds in most cases under continental anticyclones, and from the northwest with the approaching of tropical cyclones. I do not think that the winds during O3 episodes can be simplified as easterly, so did the other characteristics which were discussed as an integration in this paper.

Response: In comparison with general conditions, prevailing winds during episodes are more easterly, as shown in Fig. S5 (also provided below). We are not saying that the winds were always from the east during ozone episodes. Slight shift to northeasterly or southeasterly would not change the conclusion from the conceptual model that southwestern PRD around DH, ZML and TJ stations is a sink region of ozone produced around the Pearl River Estuary, thereby having high ozone levels during episodes. Northwest wind by the approaching of tropical cyclones could bring ozone episodes to HK and Shenzhen as they are located downwind of central PRD. However, from an entire region point of view, northwest wind during ozone episodes is rather limited.

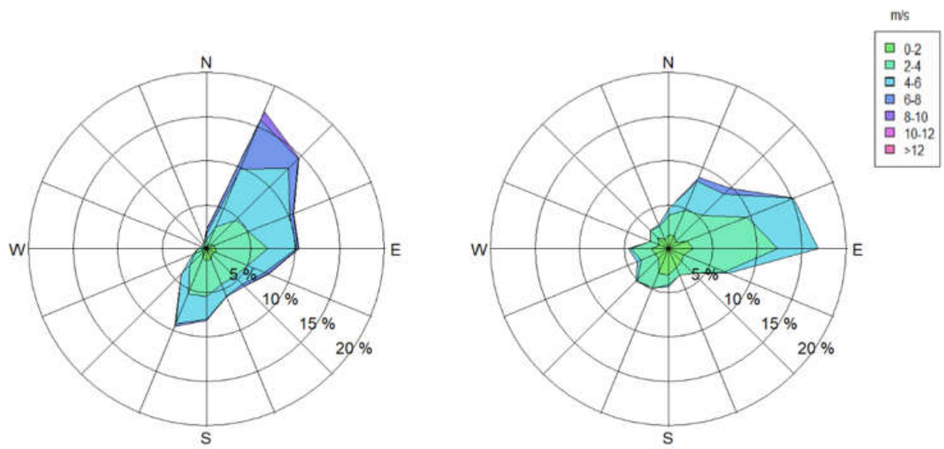

Fig S5. Wind rose under general conditions (left) and during ozone episodes (right) during 2007 and 2017 in the Pearl River Delta.

10. Page 13, lines 529 – 530. The term "optimal effective NOx/VOC ratio" needs to be annotated. The optimal ratio in fact means highest O3 production rates, which is the worst from the angle of O3 pollution control.

Response: Here we are exactly talking about NO_x/VOC ratio with highest O_3 production rate. Our previous publication (Ou et al., 2016) concluded that in the VOC-limited regime, O_3 reduction can be possible in short-term but cannot reduce O_3 into attainment. The only way is to control NO_x emission so as to change ozone formation regime from VOC-limited to NO_x-limited. In this process, O_3 concentration would increase slightly in the beginning, and drop significantly after bypassing the turning point with the optimal effective NO_x/VOC ratio that corresponds with the highest O_3 level.

References

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