Response to Referee 2

A review report on "Oxidative capacity and radical chemistry in the polluted atmosphere of Hong Kong and Pearl River Delta region: analysis of a severe photochemical smog episode" by Xue et al. (2016)

The study investigates the atmospheric radical budgets in the Hong Kong and PRD region, using a box model constrained with a full suite of ancillary measurements, not including OH or HO_2*. So, the budget analysis presented here is based solely on simulated* OH/HO_2*.*

My major concern is that the study does not provide new scientific results, especially given that several previous studies addressed this issue in the last decade, as also mentioned in the study. In addition, the inconsistency between simulated OH/HO_2 *and those previously measured in the same region weaken the results of this study and its argument toward a science-based control strategy. Add to this, several consistencies in the discussion of the results. The sensitivity analysis needs to be redone and reevaluated (see below).*

The authors should address the following issues before the Manuscript can be considered for publication.

Response: we thank the reviewer very much for the critical comments which would definitely help us to improve our work. The major concerns of the reviewer are on (1) the significance of the scientific results given lack of HO_x observations and (2) the reliability of the sensitivity analyses. Below we first address these major concerns and then reply individually the specific comments. For clarity, the reviewer's comments are listed below in black italics, while our responses and changes in manuscript are shown in blue and red, respectively.

(1) On the significance of this study

We agree with the reviewer that the present study is only based on the simulation of RO_X radicals with a full suite of ancillary observations. Without direct RO_X measurements (which are still not available so far in Hong Kong), it is difficult to address the potential 'missing' recycling pathways of HO_X radicals. Here we just would like to state the **rationale** of this study, which is to **identify the major species and reaction pathways controlling radical**

chemistry based on the 'Known Chemistry' as well as comprehensive measurements of related species/parameters. We think these results should be helpful for better understanding the atmospheric oxidation chemistry in the high-NO_X environment of Hong Kong.

Indeed, several interesting studies have demonstrated higher than can be predicted levels of HO_X at two rural sites (somewhat with low-NO_X) in the PRD region. To our knowledge, the present study appears to be the first effort to comprehensively quantify the radical budget in Hong Kong, which is generally featured by the high-NO_X condition. Previous studies have suggested that current models are usually capable of predicting the measured HO_X under the high-NO_X condition. Hence **our study may add some new information about the radical chemistry (*e.g.*, major radical sources) in the high-NO_X environment of the region**.

Moreover, an interesting result of this study is **the potential role of NO_3 in the daytime under certain conditions**. We found in one case that NO_3-initiated oxidation of VOCs was a considerable RO_X source when the solar radiation was attenuated, possibly by high aerosol pollution. This source has not been considered to be important in earlier studies. This result suggests the possible impact of daytime NO_3 oxidation in the polluted atmospheres under conditions with co-existence of abundant O_3, NO_2, VOCs and particles, which is common in the metropolitan areas and fast developing regions (*e.g.*, China).

Overall, although the present study doesn't address the 'discrepancy' between observed and modeled HO_X concentrations as found in other areas of the PRD region, it provides some new insights into the radical (RO_X and NO_3) chemistry, i.e., major primary sources of RO_X and potential role of NO_3 in daytime chemistry, in the high-NO_X environment of Hong Kong. These results should be useful for the community to understand the atmospheric chemistry in different metropolitan areas of the world.

(2) On the reliability of the sensitivity analyses

The rationale of the sensitivity analyses is to examine the sensitivity of primary radical production (**not the concentrations**) to the controllable precursors (e.g., NO_X and VOCs). We agree with the reviewer that it is irrelevant to try to reduce the atmospheric oxidation capacity. Thus the sensitivity analyses have been removed from the revised manuscript.

Abstract:

Page 1, Line 29*: The statement "Sensitivity studies show that controlling aromatics is the most efficient way to reduce the atmospheric oxidative capacity and mitigate photochemical pollution in Hong Kong." does not seem correct. The atmospheric oxidation capacity is the total loss rate of all species and thus represents the atmospheric capacity to reduce/degrade the atmospheric pollutants. Thus, I think it is just irrelevant to try to reduce the atmospheric oxidation capacity.! Reducing the photochemical pollution caused by ozone and PAN, photochemical secondary products, require sensitivity analysis to determine the contribution of each VOC to ozone formation (based on their kinetic and mechanistic properties) and target these species, which often require the use of a region‐specific reactivity scale.*

Response: we agree the point of the reviewer that it is irrelevant to try to reduce the atmospheric oxidation capacity. This sentence and sensitivity analyses (Section 3.5) have been deleted from the revised manuscript.

Page 7, line 10*: The statement "abundant VOCs would facilitate efficient radical recycling" needs revision, since the efficient recycling of peroxy radical ($RO_2/HO_2+NO=OH$) requires only reasonable amount of NO. Under VOC-sensitive conditions, higher VOC will lead to higher ROx productions.*

Response: agree. This statement has been revised as follows.

"High abundances of O_3, HONO and carbonyls would definitely lead to strong production of RO_X radicals, and the abundant VOCs would facilitate efficient radical propagation (e.g., $OH \rightarrow RO_2$)."

Page 7, Line 22*: I do not see the wind direction in Fig. S2?*

Response: wind sectors have been plotted in the revised figure. Note that Figure S2 has been moved to the main manuscript by replacing the original Figure 1. To clearly show the airmass switch, moreover, back trajectories have been shown day by day throughout the measurement period in the supplementary materials of the revised paper.

Page 8, lines 8*: would be also informative if the authors could compare these AOC values* *with other world regions from previous studies and show its significance.*

Response: the literatures about such kind of modeling AOC analysis are not too much. We compared our results with the available previous studies. The AOC values in Hong Kong were much higher than those determined at a rural site in Germany (e.g., 24-h average of 2.6×10^6 molecules cm^{-3} s^{-1}; Geyer et al., 2001), but lower than that determined at a highly polluted site of Santiago, Chile (e.g., maximum of 3.2×10^8 molecules cm^{-3} s^{-1}; Elshorbany et al., 2009). The following statement has been added in the revised manuscript.

"Such levels of AOC at TC are much higher than those determined from a rural site in Germany (Geyer et al., 2001), but a bit lower than that assessed from a polluted area in Santiago, Chile (Elshorbany et al., 2009)."

Geyer A., Alicke B., Konrad S., Schmitz T., Stutz J., Platt U.: Chemistry and oxidation capacity of the nitrate radical in the continental boundary layer near Berlin, *J Geophys. Res.*, 106, 8013-8025, 2001.

Elshorbany, Y. F., Kurtenbach, R., Wiesen, P., Lissi, E., Rubio, M., Villena, G., Gramsch, E., Rickard, A. R., Pilling, M. J., and Kleffmann, J.: Oxidation capacity of the city air of Santiago, Chile, Atmos Chem Phys, 9, 2257-2273, 2009.

***Page 8, lines 19**: Please show j(O1D) on the same figure with OH/HO_2 (figure 5).*

Response: in the present study, $J_{(O1D)}$ was not in-situ measured and was only scaled with the measured J_{NO2} in the model. In the revised manuscript, we have plotted the measured J_{NO2} values along with OH and HO_2 in Figure 5 (note that Figure 5 has been moved to the SI).

***Page 8, lines 29−33**: So, now I see some comparisons but it is not consistent with the study's results. The simulated OH/HO_2 are about 2 times lower than the measured OH/HO_2 at PRD (Hofzumahaus et al., 2009).*

Response: yes, our simulated concentrations of OH/HO_2 are much lower than the measured levels at a rural site in the northern PRD. The discrepancy may be due to the difference in the sites/environments (e.g., high-NO_X condition at TC and somewhat low-NO_X condition at BG) and/or the deficiency of current models to understand the radical chemistry (e.g., the missing recycling pathways of HO_X radicals). Without direct observations of RO_X, it is impossible to address such discrepancy between measured and modeled radical levels, which is usually found in the low-NO_X environments. As stated above in the response to major concerns, the rationale of this study is to identify the major species and reaction pathways affecting the radical chemistry in the high-NO_X environment of Hong Kong and PRD region, based on the 'known chemistry' as well as comprehensive measurements of related species and parameters. We have stated the rationale and limitation of our study in the revised manuscript. Direct measurements of RO_X radicals are quite needed to better understand the potential 'missing' pathways of radical chemistry.

Page 9, line 1*: Figure 6(a): Since the contributions of the photolysis of H_2O_2, HNO_3, OVOCs seem extremely low that is not even seen on the figure, why they are shown?*

Response: the contributions of photolysis of H_2O_2, HNO_3 and OVOCs have been removed from the revised figure, and only the major sources are shown now.

The contribution of HONO photolysis in this figure should be only the net HONO (subtract [HONO]pss from OH+NO=HONO since it is not a net OH source).

Response: this figure has been revised as suggested by only showing the contribution of net HONO (subtracting [HONO]pss).

Page 9, lines 25-35*: The authors should discuss if the mentioned heterogeneity in the primary sources is just a result of not measuring all sources (i.e, HONO was not measured in all these mentioned studies) rather than differences in regional source contributions.*

Response: we have reviewed these previous studies again. HONO was measured in most of these studies by various techniques including LOPAP, LP-DOAS and wet chemistry method. In three of these earlier efforts, i.e., Griffin et al. (2004) and Emmerson et al. (2005 and 2007), HONO was not measured and was only simulated with a chemical box model. In the revised manuscript, we have deleted the old reference of Griffin et al. (2004; their measurements were conducted in 1993), and added the following statement to clarify the difference in the observations.

"It is worth noting that HONO was not measured at Birmingham and Chelmsford but only simulated by a chemical box model, and thus the contributions of HONO photolysis were likely underestimated."

***Page 11, lines 22-25**: Why measured HONO is not constrained. The simulated HONO by the model represents only the [HONO]pss (OH+NO=HONO, HONO+hv=OH+NO) and does not represent a net source of radicals. [HONO]pss is a direct gas phase reaction of OH+NO and is not as secondary oxidation product. Not including measured HONO will certainly underestimate the simulated OH and thus will affect the simulated secondary products (e.g.,* O_3*).*

Response: we are sorry that the original description is not clear enough. Our model took into account the heterogeneous formation of HONO from reactions of NO_2 on ground and aerosol surfaces. To assess the impacts of NO_2 (partly through heterogeneous formation of HONO) on primary radical production, the measured HONO was not constrained in the sensitivity model runs. Anyway, **the sensitivity analyses have been deleted in the revised manuscript** as we agree with the reviewer that it is irrelevant to try to reduce the atmospheric oxidative capacity.

***Page 11, line 32**: The discussion in this paragraph is not clear, how decreasing* NO_2 *would decrease OH? Decreasing the OH loss via* $OH+NO_2$ *reaction (via decreasing* NO_2*) should lead to increased OH. Decreasing NO (only NO) would decrease OH (via decreasing the reaction rate of* $RO_2/HO_2+NO=OH$*).*

Response: we are sorry that this section is not clear. By the sensitivity studies, we focused on the primary production of radicals, NOT the concentrations. We meant that decreasing NO_2 would decrease the primary production of OH by decreasing the heterogeneous formation of HONO. Anyway, **the sensitivity analysis (Section 3.5) has been deleted in the revised manuscript**, see above.

***Page 11, line 33**: The authors did not mention before if they included a mechanism for heterogeneous formation of HONO? How this was considered parallel to measured HONO?*

Response: we are sorry that we didn't clearly state this, which made the manuscript confusing. Our model includes the heterogeneous formation of HONO from reactions of NO_2 on ground and aerosol surfaces. In the revised manuscript, a detailed description of the model has been provided in the supplementary materials. Again, this section has been deleted in the revision.

How reducing NOx would decrease OH (line 32) and increase O_3 (line 34)?

Response: as stated above, reducing NO_X would decrease the primary OH production (NOT the concentration) via decreasing the heterogeneous formation of HONO. According to our sensitivity studies, the O_3 production at TC is highly VOC-limited and in a NO_X-saturated regime. Reducing NO_X would lead to increased O_3 by weakening the NO titration. Again, this section has been removed from the revised manuscript.

Page 11, line 34*: What is a "NOx-titrated regime", it's not defined anywhere in the text?*

Response: as stated above, this discussion has been removed from the revised version.

Minor comments:

Could the authors address the differences between the MCMv3.2 and the most recent version, and how this would affect their analysis?

Response: the updates of MCM *v3.3.1* against the MCM *v3.2* are mainly on the chemistry of biogenic VOCs, including the degradation of isoprene and ozonolysis rate constants of α/β-pinenes, limonene, and β-caryophyllene. As our site (TC) is primarily influenced by the anthropogenic pollution, and the levels of BVOCs are indeed much lower than the AVOCs. Thus the impact of different versions of mechanism should be small on the analyses in the present study.

We have rerun the model with the MCM v3.3.1, and examined the difference in the simulated primary OH production rates between both mechanisms (note that we don't conduct the same analyses as the present study with the latest version of MCM, as it is really a huge work to track more than 15000 reactions in the model within a short period). As shown in the figures below, the differences between both versions of MCM are quite small.

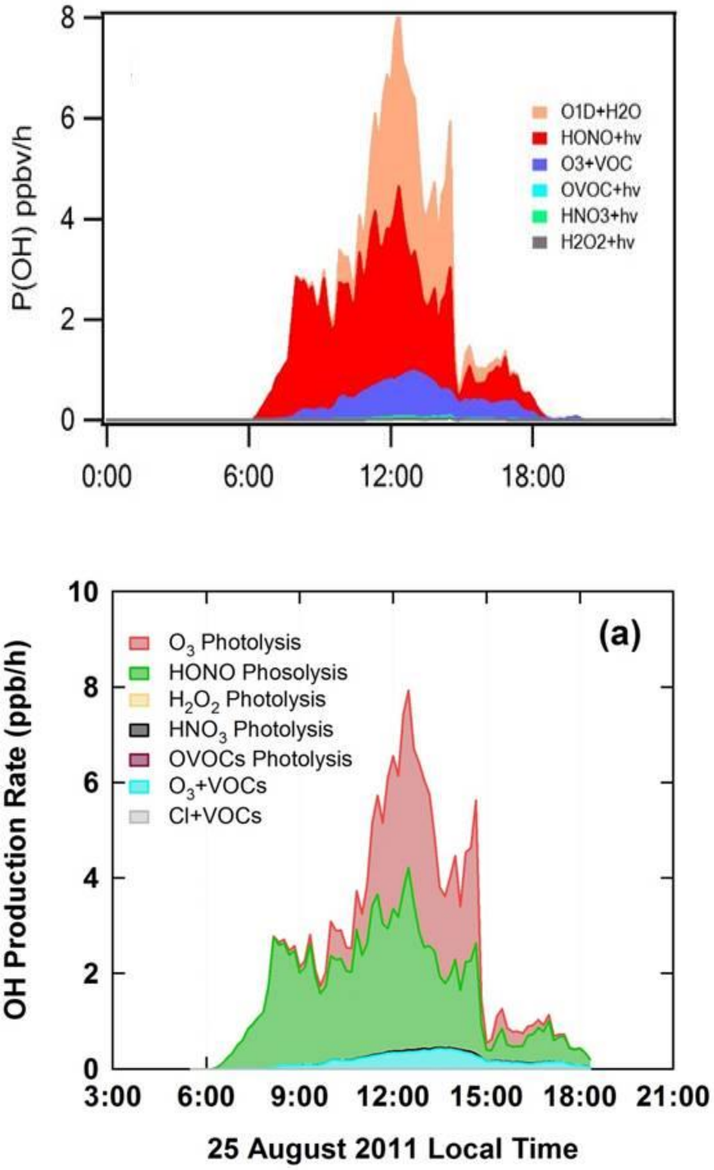

Figure 1. The modeled primary production rates of OH at TC on 25th August 2011 with the MCM *v3.3.1* (top panel) and the MCM *v3.2* (bottom panel). **Note that the legends and scales of y-axis are different for both plots**.