Response to referee's comments

This manuscript presents a modelling case study of the oxidative capacity of Hong Kong and the Pearl River Delta region of China during a photochemical smog episode. The dominant ROx radical sources and OH sinks are identified. NO_3 *is identified as a non-negligible ROx source during the daytime when solar irradiation was attenuated by high aerosol loadings. This is an interesting result, and this source of ROx has not been considered to be important in earlier studies. Through sensitivity analyses, a reduction in the loading of aromatics is highlighted as an efficient way to mitigate photochemical pollution. This paper demonstrates nicely the major species and reaction pathways which control the oxidation chemistry in this region, however, there is a lack of synthesis of the results and discussion on the impact of these findings, and how these findings compare to previous urban studies is limited. In addition to a number of minor comments, I have made a number of suggestions below on where more detail is warranted or where the discussion should be developed before final publication is considered.*

Response: we appreciate the reviewer for the positive comments and helpful suggestions. In the revised manuscript, we have addressed all of the comments, and particularly adopted the suggestion to synthesize our results and compare against existing findings of previous studies. The manuscript has been significantly revised and improved based on these suggestions. 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.

Pg 1, line 16: 'we analyze a multi-day photochemical smog episode.' Actually the analysis is confined to two individual days.

Response: the original phrase has been changed as below.

"We analyze a photochemical smog episode…"

Pg 2, line 12: remove the space between the arrow and 'RO'.

Response: done.

Pg 2, lines 18 – 29: Some care is needed when discussing the relative primary radical *sources at different urban sites: In some of the earlier studies HONO was not measured (e.g. Emmerson et al, 2005) and the inability of models to reproduce observed daytime HONO concentrations means that some of the differences observed may be caused by differences in model constraints. The model constraints used in these studies should be considered here along with the differences highlighted. Some comment on the relative source strengths in ppb/hr would be helpful and could be referred to when the results from the TC study are discussed.*

Response: we have reviewed these previous studies again. HONO was not measured in three of these earlier studies, i.e., Griffin et al. (2004) and Emmerson et al. (2005 and 2007). In the revised manuscript, we have deleted the old reference of Griffin et al. (2004; note that the measurements were conducted in 1993), and added the following statement to clarify the difference in the model constraints.

"Note that HONO was not in-situ measured but simulated by a box model in Emmerson et al. (2005 and 2007), and hence the contributions of HONO photolysis might be underestimated."

Pg 4, line 18: Define 'MoO'.

Response: defined.

Pg 5, line 1: Although a reference is provided which relates to the differences between the on-line and canister alkene measurements a comment should be made in this manuscript on why the canister sample are considered more reliable than the on-line measurements.

Response: the canister measurements had much lower detection limits (i.e., 3 pptv), while the detection limits of the real-time analyzer were much higher, especially for the alkene species with less carbon numbers. The description has been modified as follows, with changes being highlighted as the underlined sentences.

"C_2-C_{10} non-methane hydrocarbons were measured at a time interval of 30 minutes by a commercial analyzer that combines gas chromatography (GC) with photoionization detection (PID) and flame-ionization detection (FID) (*Syntech Spectras, model GC955 Series 600/800 POCP*). <u>The detection limits for the measured VOCs ranged from 0.001 to 0.19 ppbv.</u> In addition, 24-hour whole air canister samples were collected on selected days (e.g., 25 and 29 August) for the detection of C_1-C_{10} hydrocarbons by using GC with FID, electron capture detection (ECD) and mass spectrometry detection (MSD). The analyses were carried out at the laboratory of the University of California at Irvine, and the detection limit was 3 pptv for all measured species (Simpson et al., 2010; Xue et al., 2013). As evaluated in our previous study, both sets of hydrocarbon measurements agree very well apart from the alkenes. Here the real-time data tended to systematically overestimate the canister measurements (Xue et al., 2014b). Considering the generally lower detection limit of the canister measurements, the high resolution real-time data were corrected in the present study according to the canister data."

Section 2.2 The OBM-AOCP model: Further details on model parameters are required. The reader should not have to refer to the references for parameters specific to this study. What uptake coefficients were assumed for HO_2 and N_2O_5? What deposition rate was used? Which model species were deposited? Lines 28, 29: '...impacts on the modelling results were negligible': Which model species were considered when assessing the impact of mixing height?

Response: in the revised manuscript, a detailed description about the model configuration and parameters has been provided in the supporting information. Below are brief responses to the specific questions.

The model adopted moderate uptake coefficients of 0.02 for HO_2 and of 0.014 for N_2O_5. The γ_{N2O5} was taken from the observationally-derived value from our field studies in Hong Kong (Wang et al., 2016).

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Dry deposition was considered for various inorganic gases and organic species such as PANs, peroxides, carbonyls and organic acids. The dry deposition velocities were adopted from the literature of Zhang et al. (2003).

Zhang, L., Brook, J. R., and Vet, R.: A revised parameterization for gaseous dry deposition in air-quality models, *Atmos. Chem. Phys.*, 3, 2067-2082, doi: 10.5194/acp-3-2067-2003, 2003.

When assessing the impact of assumed mixing height on the modeling results, we examined the changes of HO_X concentrations and OH production rates between base and sensitivity model runs. The original statement has been modified as below.

"Sensitivity model runs with different maximum mixing heights (1000 and 2000 m) indicated that its impacts on the modeling results (e.g., simulated HO_X concentrations and OH production rate) were negligible."

How was H_2 treated in the model? Was this measured?

Response: H_2 was not measured. An initial concentration of 0.5 ppm of H_2 was assumed in the model. A description has been added in the revised manuscript on the H_2 treatment.

Are all the VOCs listed in Table 1 used as model constraints? Does this equate to 15600 reactions or does this figure refer to the number of reactions when the MCM is run in its entirety?

Response: yes, all the VOC species listed in Table 1 were used as model constraints. The full MCM was used in the model, and the figure "15600" refers to the number of reactions whose rates were tracked in our model. In the present study, with only a subset of primary MCM VOCs used as model constraints, the actual number of valid reactions should be smaller (the rates of some reactions should be zero). The original statement has been revised as follows.

"In our model, the rates of over 15600 reactions out of the full MCM (v3.2) are individually and instantaneously computed and grouped into a relatively small number of major routes."

*Pg 5, Line 33: It is unclear what the authors mean by '..and grouped into a relatively small number of major routes'. Does this grouping take place post-*model run*? I think this sentence needs re-wording so it is clear to the reader what analysis this relates to.*

Response: no, this grouping is done in the model. A module was introduced in the model to do this. For clarity, this sentence has been modified as follows in the revised version.

"In our model, the rates of over 15600 reactions out of the full MCM (v3.2) are individually and instantaneously computed and grouped into a relatively small number of major routes."

Pg 6, line 17: Change 'simulation' to 'comparison'

Response: it has been rephrased to "calculation", as we don't compare modeling results with observations.

Pg 6, line 18: what is meant by 'reasonable estimates'? Do the authors mean until steady state conditions are reached?

Response: yes. It means the steady state conditions. This sentence has been changed as follows.

"Prior to formal calculation, the model was run for five days with constraints of the campaign-average data to reach steady states for the unconstrained compounds (*e.g.*, radicals)."

Pg 6, line 26: The authors should consider replacing Figure 1 with the similar figure provided in the supplementary information (Figure S2) which highlights the contrasting conditions well and provides more information than presented in Figure 1.

Response: replaced as suggested, and Figure 1 was moved to the supplementary information.

Pg 6, line 30: Remove 'meanwhile'

Response: done.

Pg 6, line 33: '…intense photochemical oxidant production' this figure does not demonstrate this, rather, the subsequent model analysis reveals this.

Response: the original sentence has been rephrased as below. The phrase "photochemical oxidant production" is changed to "photochemical pollution", as high levels of O_3 and PAN were observed.

"Overall, inspection of the data reveals the markedly poor air quality and serious photochemical pollution over the region during the episode.”

Pg 7, line 3: Need to contrast these concentrations with other relevant observations, e.g. perhaps typical concentrations measured at other urban centers or could contrast with the concentrations of these species observed at TC prior to the pollution episode.

Response: these VOC concentrations were much higher than those observed during the non-episode period. For example, the 24-h average concentrations (±SD) of toluene and xylenes during the non-episode period were 0.80 ±0.03 and 0.13 ±0.01 ppbv, compared to the levels of 9.47 and 3.87 ppbv on 25 August. The measured concentrations of formaldehyde and acetaldehyde were 3.25 and 0.83 ppbv during a non-episode day (*i.e.*, 6 September; note that we only had OVOC measurements on that day during the non-episode period), compared to 9.89 and 4.25ppbv on 25 August. The following statement has been added in the revised manuscript.

“On 25 August, for instance, the 24-h average values of toluene, summed xylenes, formaldehyde and acetaldehyde were as high as 9.47, 3.87, 9.89 and 4.25 ppbv, which were 3–30 folders higher than those measured during the non-episode period of the campaign (figures not shown).”

Pg 7, line 6: Elevated daytime HONO concentrations at urban locations that cannot be reproduced by models which consider only gas-phase chemistry are now well reported. So not uncommon, but interesting nonetheless.

Response: yes, we agree. The present study didn’t focus on the unknown sources of daytime HONO, and only evaluated the role of HONO photolysis as a radical source.

Pg 7, line 14: Is the Ding et al. 2004 reference appropriate given that it was published before this campaign so cannot document the source of the pollution event discussed here.

Response: the reference has been deleted from the revised manuscript.

Pg 7, line 20: I suggest moving figure 2 to SI. It is not critical for the paper, unlike some of the other figures currently in the SI (see later comments). Is there an order to the trajectories shown? Does Red = 25th? It would be helpful to highlight the PRD region on the map.

Response: Figure 2 has been moved to the SI as suggested. It is further improved by labeling the trajectories and indicating the PRD region on the map. Yes, the red one is the trajectory on 25th August.

Pg 7, line 22: Fig S2 does not highlight this airmass switch discussed. Should another figure be referenced here?

Response: wind sectors have been added on this figure (note that Figure S2 has been moved into the main manuscript). To clearly show the air mass switch, back trajectories have been shown day by day throughout the measurement period in the supplementary materials of the revised paper.

Pg 8, line 5: What is the % contribution of NO_3 during the day on the 31st August? Which VOC species is NO_3 primarily oxidizing? The authors suggest that ozonolysis isn't significant here because of the 'lower abundances of alkenes' so I presume carbonyls dominate NO_3 reactivity? More detail needed on this.

Response: the contribution of NO_3 to the AOC was approximately 3% on 31st August. The major VOC species oxidized by NO_3 at TC were OVOCs and alkenes, with daytime average contributions of 77%-90% and 10%-23% respectively. The following discussion has been added in the revised manuscript.

"NO_3 was the second important oxidant with contributions of 7% and 3% for both cases. In particular, NO_3 contributed to 43% of the AOC at 15:00 LT on 25 August under a weak solar radiation condition. The major 'fuels' for NO_3 oxidation were OVOCs (i.e., 77%–90%) and alkenes (10%–23%)."

How does figure 3 compare to similar analyses reported in the literature? E.g. Bannan et al. (JGR-Atmos, 2015).

Response: the following statements have been added in the revised manuscript to compare our results with the other similar studies.

"Overall, the OH-dominated AOC at TC is in line with the previous studies at other urban locales (Elshorbany et al., 2009; Bannan et al., 2015), and the present analysis suggests that the NO_3 radical may play an important role in the daytime oxidation under certain conditions (see a detailed evaluation in Section 3.4)."

Pg 8, line 8: Is Nitryl chloride the only source of Cl atoms in the model? What was the daytime concentration of Cl atoms predicted? Please state. How was the photolysis rate of $ClNO_2$ (and the photolysis of other Cl-containing species) incorporated into the model?

Response: yes, $ClNO_2$ photolysis was the only source of Cl atoms in the model. The modeled concentration of Cl atoms was relatively low with peak values of $\sim 1\times10^4$ atoms cm^{-3}, due to the moderate/low levels of $ClNO_2$ and/or weak sunlight. The photolysis frequency of $ClNO_2$ (J_{ClNO2}) was calculated in the model as a function of J_{NO2} ($J_{ClNO2} = 0.04\times J_{NO2}$). The treatment of photolysis of $ClNO_2$ and other Cl-containing species has been provided in the detailed model description in the revised supporting information. The statement has been modified as below in the revised manuscript.

"In comparison, O_3 and Cl (produced from $ClNO_2$ photolysis) had minor contributions due to the relatively lower abundances of alkenes and Cl radicals (i.e., the modeled peak value of Cl was $\sim 1\times10^4$ atoms/cm^3)."

Pg 8, lines 9 and 10: poor sentence structure, please revise.

Response: this sentence has been revised as follows.

"We further assessed the loss rates of major VOC groups due to OH oxidation, by which the partitioning of OH reactivity among different VOCs can be elucidated."

Pg 8, line 10, figure 4: For ease of comparison with earlier reported OH reactivities at urban sites, could figure 4 be presented as a breakdown of OH reactivity with units (s-1)? i.e. divide through by modelled OH concentration.

Response: the unit in the figure has been changed as suggested.

Pg 8, lines 11–16: Does this partitioning include model-generated intermediate species in the OVOC segment? I note from Table 1 that elevated levels of isoprene were observed on the 25th (relative to the 31st), do the biogenic measured contribute significantly to OH reactivity at TC? How does this compare to the recent OH reactivity observations made in London

(Whalley et al. ACP, 2016)?

Response: yes, the OVOC segment includes both the measured carbonyls and the modeled intermediates. Although the concentrations of isoprene on 25th August were higher than those on 31st August, they are still much lower than reactive aromatics at such an urban site. The contribution of isoprene to the OH reactivity was quite small at TC, and it was already included into the alkenes segment.

Whalley et al. (2015) reported a very interesting result that biogenic VOCs and their reaction intermediates present an important contributor of the OH reactivity in central London, and explained largely the discrepancy between measured and modeled OH reactivity. Though the roles of biogenic VOCs are different, our study agrees well with Whalley et al. (2015) on the dominance of OVOCs (including carbonyls and intermediates) in the OH reactivity of VOCs. The following statement has been put in the revised manuscript.

"These results are in fair agreement with the previous studies of Lou et al. (2010) and Whalley et al. (2015), which indicated the dominance of secondary OVOCs in the observed OH reactivity in the PRD region and central London."

Pg 8, lines 19–34: without a direct comparison to ROx observations at TC specifically this commentary adds little to the manuscript and so I suggest removing this paragraph (or expand this section to provide further discussion of the dominant radical sources and sinks in the campaigns referred to – and how these sources and sinks compare and contrast with TC).

Response: we agree with the point of the reviewer, and have removed this paragraph from the main manuscript (to response the other review comments, it was moved to the supplementary materials).

Pg 9, line 3: I suggest Figs S5 and S6 are moved into the main paper.

Response: both figures have been moved into the main paper as suggested.

Pg 9, line 13: Some information on the identity of the other OVOCs which contribute to HO_2 production is needed. Are these compounds which were measured directly (e.g. acetaldehyde) or oxidation products generated by the model? How do these source strengths compare to *other urban locations?*

Response: these OVOC compounds include both the measured species (see Table 1) and the model-generated oxidation intermediates/products. Its source strength is comparable to those determined previously in Beijing (Liu et al., 2012) and Mexico City (Volkamer et al., 2010). The daytime-average source strengths were 2.4 ppb/hr (as a total of HCHO and other OVOCs) and 2.6 ppb/hr in Beijing and Mexico City, respectively. The following statements have been modified/added in the revised manuscript.

"For HO_2, the most important source is the photolysis of OVOCs (including not only the measured carbonyls but also the oxidation products generated within the model), with a daytime average production rate of 2.7 ppbv/h."

"Such source strength of OVOC photolysis was comparable to those determined in the metropolitan areas of Beijing (Liu et al., 2012) and Mexico City (Volkamer et al., 2010)."

Pg 9, line 16: 'As to' to 'For'

Response: changed.

Pg 9, lines 17–18: Considering RO_2 deriving from NO_3+VOC reactions, this source seems to have a similar % contribution to the total RO_2 sources both on the 25th when $j(NO_2)$ was attenuated and also on the 31st when $j(NO_2)$ was not attenuated. A comment is needed which compares these two contrasting days.

Response: the contribution of NO_3+VOC reaction pathway to the total RO_2 sources was 11.8% (0.2 ppb/h out of 1.7 ppb/h) on 31st August, which was lower than that on 25th August (18.5%; 0.5 ppb/h out of 2.7 ppb/h). In the revised manuscript, we have added a sub-section in Section 3.3 to discuss the radical budget on 31st August and compare against the local case on 25th August.

Pg 9, line 20: '...different from most results obtained elsewhere' a reference to support this statement is needed.

Response: a review paper of Stone et al. (2012), which comprehensively reviews the existing results of radical chemistry, has been cited in the revised manuscript. The original statement has been modified as follows in the revised manuscript.

"…different from most results obtained elsewhere which have indicated the negligible role of NO_3 in the daytime photochemistry (Stone et al., 2012; and references therein…"

Stone, D., Whalley, L. K., and Heard, D. E.: Tropospheric OH and HO_2 radicals: field measurements and model comparisons, *Chem. Soc. Rev.*, 41, 6348-6404, 2012.

Pg 9, lines 25-35: See earlier comment on model constraints in the various studies highlighted.

Response: see the response to the earlier comment. The following statement has been added here.

"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."

Section 3.3: I suggest that a discussion on how the 25th and 31st contrast be included at the end of this section, focusing on local versus regional influences?

Response: in the revised manuscript, we have added a sub-section in Section 3.3 to discuss the radical budget on 31st August and compared it with the results obtained on 25th August. The primary radical sources were essentially the same for both cases. Specifically, the major RO_X sources were photolysis of OVOCs, HONO, O_3 and HCHO, and reactions of O_3+VOCs and NO_3+VOCs. Nevertheless, the sources of photolysis of HONO, O_3 and HCHO were higher on 31st August than 25th August, whilst the sources of OVOCs photolysis, O_3+VOCs and NO_3+VOCs were stronger on 25th August compared to 31st August (see the table below). This difference should be due to the higher VOC levels and attenuated solar radiation on 25th August.

Table 1. Average daytime radical sources at TC on 25th and 31st August 2011

Source (ppb/hour)		25th August 2011 Hong Kong Local case	31st August 2011 PRD Regional case
OH	HONO photolysis	1.5	**1.7**

	O_3 photolysis	0.9	**1.5**
	O_3+VOCs	**0.2**	0.1
HO_2	Other OVOC photolysis	**1.9**	1.3
	HCHO photolysis	0.8	**1.2**
	O_3+VOCs	0.1	0.1
RO_2	Other OVOC photolysis	**1.9**	1.3
	NO_3+VOCs	**0.5**	0.2
	O_3+VOCs	**0.2**	0.1
	Cl+VOCs	0.1	0.1

Pg 10, line 23: I am not sure that RH can be used to confirm cloud-cover. Does it matter what caused this attenuation?

Response: the relatively low RH is indicative of little cloud on the site, but may not refer to the cloud cover at higher altitudes. The original statements have been modified as follows in the revise manuscript.

"The ambient relative humidity (RH) in the afternoon was in the range of 60%-70%, implying that there was little cloud on the site, whilst the aerosol scattering coefficient was very high (up to 525 Mm^{-1}; compared to 28±12 Mm^{-1} on clear days). Hence, the attenuated solar radiation is possibly attributed to the abundant aerosol loadings."

Pg 10, line 30, Fig. 9: Please include the modelled heterogeneous loss rate of N_2O_5 in this figure. What uptake of N_2O_5 was assumed?

Response: the modelled heterogeneous loss rate of N_2O_5 has been included in the revised figure. The model adopted a moderate uptake coefficient of 0.014 for N_2O_5. The γ_{N2O5} was taken from the average observationally-derived value from our field studies in Hong Kong (Wang et al., 2016).

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Pg 11, line 1: Does the high aerosol loading impact the heterogeneous loss of N_2O_5*?*

Response: yes, but the model was constrained by the measured aerosol surface area data. Thus the impact of high aerosol loading on the heterogeneous loss of N_2O_5 had been taken into account in the present analysis.

Section 3.5: I found this section difficult to follow as the sentence structure was poor throughout. This needs a careful edit to improve the clarity.

Response: this section has been deleted from the revised manuscript, based on the other review comment.

Pg 11, lines 32 – 33: '...due to the attenuated heterogeneous formation of HONO'. Were heterogeneous sources of HONO included in the model? If they were, a description of these sources should be included in the experimental description. If they were not included, then attenuated heterogeneous formation of HONO cannot be the cause of the reduction of OH in the model. Is this trend not simply caused by a reduction in the secondary OH source from HO_2*+NO? In this analysis are NO and* NO_2 *concentrations both reduced by the same fraction?*

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. As stated above, anyway, this section has been deleted from the revised version.

Why were only alkanes, alkenes and aromatics considered in this analysis? What is the sensitivity to the other VOC groups measured, e.g. the Biogenics?

Response: as stated above, the sensitivity studies have been deleted in the revised manuscript.

Conclusions: This section should provide some commentary on the local versus regional events; the latter sections of the paper neglect the case study on the 31st and it would conclude the paper nicely if the results from this day were evaluated alongside the 25th here.

Response: in the revised manuscript, we have added a discussion of the case study on 31st

August (see the responses above). The following sentences have also been added in the conclusion section to state the difference between the two cases.

"Higher AOC levels and stronger primary production of radicals were determined during the Hong Kong local case compared to the PRD regional case. Although the primary radical sources were essentially the same, photolysis of OVOCs (except for HCHO) and reactions of O_3+VOCs and NO_3+VOCs were stronger for the local case, which was ascribed to the higher VOC levels. In comparison, the source strengths of photolysis of HONO, O_3 and HCHO were higher during the regional case."