

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 RO_x radical sources and OH sinks are identified. NO₃ is identified as a non-negligible RO_x source during the daytime when solar irradiation was attenuated by high aerosol loadings. This is an interesting result, and this source of RO_x 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.

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

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

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.

Pg 4, line 18: Define 'MoO'.

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.

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 HO₂ and N₂O₅? 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?

How was H₂ treated in the model? Was this measured?

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?

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.

Pg 6, line 17: Change ‘simulation’ to ‘comparison’

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

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.

Pg 6, line 30: Remove ‘meanwhile’

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

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

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.

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.

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.

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

Pg 8, line 5: What is the % contribution of NO₃ during the day on the 31st August? Which VOC species is NO₃ primarily oxidising? The authors suggest that ozonolysis isn’t significant here because of the ‘lower abundances of alkenes’ so I presume carbonyls dominate NO₃ reactivity? More detail needed on this.

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

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 ClNO₂ (and the photolysis of other Cl-containing species) incorporated into the model?

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

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.

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 biogenics 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)?

Pg 8, lines 19 – 34: without a direct comparison to RO_x 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).

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

Pg 9, line 13: Some information on the identity of the other OVOCs which contribute to HO₂ 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?

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

Pg 9, lines 17 – 18: Considering RO₂ deriving from NO₃+VOC reactions, this source seems to have a similar % contribution to the total RO₂ sources both on the 25th when $j(\text{NO}_2)$ was attenuated and also on the 31st when $j(\text{NO}_2)$ was not attenuated. A comment is needed which compares these two contrasting days.

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

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

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

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

Pg 10, line 30, Fig. 9: Please include the modelled heterogeneous loss rate of N₂O₅ in this figure. What uptake of N₂O₅ was assumed?

Pg 11, line 1: Does the high aerosol loading impact the heterogeneous loss of N₂O₅?

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.

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 $\text{HO}_2 + \text{NO}$? In this analysis are NO and NO_2 concentrations both reduced by the same fraction?

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?

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.