

Responses to Referee #1

This paper provides a detailed study of trace gases and meteorology at two sites, one a suburban site in Hong Kong (labelled TC), the other a coastal site (labelled WS), with few local anthropogenic emissions, on the edge of the South China Sea. The sites are separated by ~ 40 km. Emphasis is given to ozone episodes (>100 ppbv) and near episodes, which occurred on a number of occasions, some extending over 9 days, during two ~50 day periods in August, September; October, November 2013. The results are rationalised in detail using a range of modelling techniques: a zero dimensional box model study using the master chemical mechanism (MCM); the Weather Research and Forecasting (WRF) model to provide wind fields and coupled with the CMAQ model to provide an Eulerian representation of the physical and chemical processes over a wide area and HYSPLIT to provide backward particle release simulations to understand air mass origins. The paper provides a very useful dataset and an interesting analysis.

Thanks for the positive comments and the concerns, which helped to improve the manuscript substantially. Responses are given item by item below following the specific comments, and revisions are made where necessary.

1. The results are discussed in terms of the interaction between marine and continental air. The episodic ozone concentrations are significantly higher at WS than at TC and much of the paper relates to a discussion of the origin of these differences, which are ascribed to weaker NO titration and to a stronger oxidative capacity at the coastal site. The main meteorological features during the episodes were tropical cyclones, with transport from the polluted Pearl River Delta Region to the sites, continental anticyclones, which again brought air from polluted inland areas and Sea Land Breezes, with alternation of onshore and offshore winds.

My main concern is with the contention that the results relate to the interaction between marine and continental air, which is included in the title and pervades the text. WS is one of several islands lying close to the coast. Its important characteristic is that there are few local emissions so that NO_x is low. Other pollutants, CO, SO₂, NMHC show clear indications of advection of polluted air, but the concentrations are on average

lower than those found at TC. The wind patterns confirm that the air is primarily, perhaps exclusively during the episodes, of continental origin. Even the SLB winds from the sea simply advect high ozone concentrations, formed in polluted air, back to the coastal region. Marine air has much less impact than is found and has been widely discussed at, say, Mace Head in Ireland or Cape Grim in Tasmania.

The excellent comment is highly appreciated. As presented in the manuscript and summarized by the referee, this paper focused on the interaction between the continental and marine air in the coastal area of Hong Kong. The impacts of the continental air on air quality in marine boundary layer were discussed profoundly. Specifically, the polluted continental air masses were transported to the marine atmosphere under tropical cyclone, continental anticyclone and land breeze (section 3.2). As a result, the chemical compositions of the marine air changed substantially, leading to increased O₃ production under northerly winds at the reception of continental air (section 3.3). This process was further confirmed by the chemical transport model (section 3.4).

However, as concerned by the referee, we agree that the impacts of marine air on continental air quality were not discussed in such a comprehensive way. In fact, this effect was mainly described as sea breeze (section 3.2.3) and the intrusion of high O₃ formed over South China Sea into the continental area under sea breeze (section 3.4). In the revised manuscript, the alleviation of continental air pollution under oceanic flow is discussed, which represents a type of interaction between the continental and marine air. Furthermore, the enhancements of oceanic emission tracers (*e.g.* dimethyl sulfide) in the inland area under sea breeze are presented as an indication of marine influence. This is consistent with the findings at Mace Head in Ireland and Cape Grim in Tasmania. At last, what we want to emphasize is that this study focuses on O₃ pollution under the interaction between continental and marine air. The advection of marine air laden with O₃ back to the coastal areas is a typical interaction in this region, which is thought to be an important marine influence.

Revisions are made in the revised manuscript as follows.

The arrival of oceanic air masses generally brings substantial marine-originated compounds (e.g. dimethyl sulfide) to the continent and significantly alleviates the anthropogenic air pollution there. In fact, this is one of the main reasons for low O₃ mixing ratio observed in the PRD region in summertime when southwestern winds prevail (Wang et al., 2009; Wang et al., 2017a). In this study, it was also found that winds over the ocean increased the concentration of dimethyl sulfide at TC (see Figure S8) and reduced the levels of almost all man-made air pollutants in many cases, mainly in summertime (Figure 2a). In contrast, sea breezes carrying elevated O₃ formed over SCS might build up the terrestrial O₃ in the coastal area in some cases.

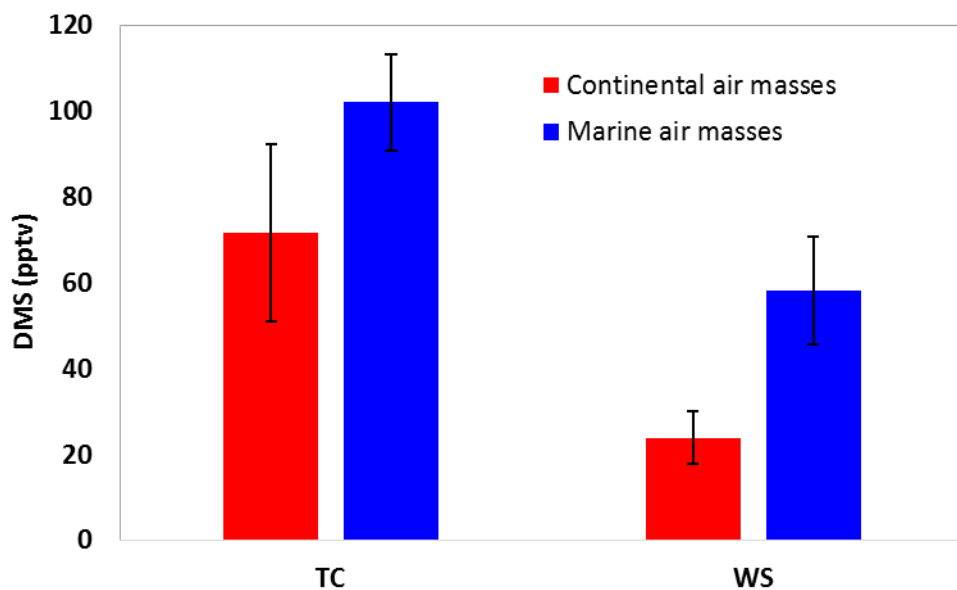


Figure S8 Average concentrations of dimethyl sulfide (DMS) observed at TC and WS when continental or marine air masses dominate.

For details, please refer to Page 29, Lines 2-11 in the revised manuscript and in the supplement.

2. The observation of higher ozone at WS compared with TC derives primarily, as argued, from the low emissions at WS and the consequently much lower NO_x and reduced titration via NO + O₃. The most telling observation is the near equivalence of

the total oxidant concentration at the two sites during both episodes and non-episodes (p 20). Similar behaviour is of course found in many other locations when comparing rural and urban ozone concentrations in similar air masses. It is the absence of local NO_x emissions at WS that leads to the differences; it is not specifically related to its coastal location and certainly not to marine influences.

Thanks for the comments. We agree that, due to the influence of NO titration, the near equivalence of the total oxidant concentration is common between two sites where primary air pollutants are intensively emitted at one site and then transported to the other site. Indeed, the similar behavior at WS and TC was partially attributable to this effect (see section 3.3.2). However, this study also demonstrated that the more intensive in-situ O₃ formation due to the stronger oxidative capacity of the atmosphere could be another important factor for the higher O₃ at WS (see section 3.3.3). Additionally, O₃ formed during the transport of polluted air masses from the continent to the marine atmosphere might also elevate O₃ at WS, which will be discussed in a companion paper (Wang et al., 2018). In fact, wherever the observed O₃ was formed, *i.e.* at WS or during the transport of air masses from the inland area to WS, the high O₃ at WS was a reflection of the interaction between the continental and marine air, because WS was nearly free of anthropogenic emissions where O₃ and its precursors were originated from the continent. Certainly, this interaction was mainly manifested as the impacts of continental air on marine air quality. We understood that the marine influences should be emphasized as a part of interaction between the continental and marine air. As responded to the previous comment (comment #1), discussions on the marine influences are extended in the revised manuscript.

3. The discussion of the daily ozone profile could also be improved. The diurnal variation is superimposed on a residual night-time ozone concentration, which is substantial, Figs 2 and S4. This might be discussed.

Many thanks for the comment. The suggested discussion has been provided in the revised manuscript.

In this study, the average NO mixing ratio at TC was 14.0 ± 0.8 ppbv, compared to 0.7 ± 0.1 ppbv at WS (Table 1). The much lower NO at WS implied weaker titration to O₃, which enabled the survival of more O₃ and caused substantial residual O₃ at WS particularly at night time when there were no photochemical reactions (Figure 2 and Figure S6).

For details, please refer to Page 21, Lines 9-12.

4. Is the higher rate of ozone formation, shown in Fig 5b, a reflection of the high ozone concentration itself? It would be helpful to show the concentrations of OH, HO₂ and RO₂ vs time and also their rates of production and loss. Is the enhanced [OH] a result of increased O¹D production from the higher [O₃] found at WS in episodes? These plots could, if necessary, be shown in the Supplement.

We are grateful for the good comments. The higher net O₃ production during O₃ episodes at WS, as shown in Figure 5 (b) of the original manuscript, was directly caused by the enhanced reaction rates of RO₂+NO and HO₂+NO. This was associated with the increase of O₃ precursors, particularly NO_x, during O₃ episodes. Under the assumption that local O₃ formation dominated O₃ budget at WS, the higher O₃ production rate during O₃ episodes resulted in higher O₃, or it was a reflection of the higher O₃. However, the higher O₃ production rate was not caused by the higher observed O₃ during episodes, which were not input into the model.

As suggested, the concentrations of OH, HO₂ and RO₂, as well as their production and loss rates, are presented in the revised supplement with discussions in the revised manuscript. The enhanced [OH] during O₃ episodes cannot be totally attributable to the increased O¹D (O₃ photolysis). Instead, most of the OH increase was attributable to the enhanced reaction rate between HO₂ and NO during O₃ episodes.

O₃ formation is driven by the transformation and recycling of oxidative radicals, including OH, HO₂ and RO₂, collectively referred to as RO_x hereafter. The production and loss rates of these radicals, and their equilibrium concentrations on the canister sampling days were simulated by the PBM-MCM model, as shown in Figure S7. We noticed that WS featured significantly higher levels of these oxidative radicals on average ($p < 0.05$). The daytime (7:00-19:00 LT) average OH

concentration at TC and WS was $(1.5 \pm 0.4) \times 10^6$ molecules cm^{-3} and $(5.5 \pm 0.9) \times 10^6$ molecules cm^{-3} during O_3 episodes, respectively. Consistently, HO_2 and RO_2 at WS were well above those at TC (Table 3). This pattern was also applicable between the two sites during non-episodes. Furthermore, while the difference in OH concentration became less on non-episode days, the gaps for peroxy radicals (HO_2 and RO_2) between TC and WS widened, as listed in Table 3. From non-episodes to episodes, OH increased at WS alongside with the decreases of HO_2 and RO_2 , likely indicating more conversion of HO_2 to OH by NO, which is an important pathway leading to O_3 formation. Details about this were shown later.

To explain the inter-site differences of the concentrations of oxidative radicals and the variations between O_3 episodes and non-episodes, Figure S7 also provides the breakdowns of the production and loss rates of OH, HO_2 and RO_2 at TC and WS, separately. Overall, the reaction between HO_2 and NO dominated the production of OH at both sites, with the contribution of $69.4 \pm 2.0\%$ and $81.0 \pm 1.5\%$ at TC and WS, respectively. While the photolysis of HONO ranked the second in the production of OH at TC ($22.2 \pm 2.1\%$), the contribution of this pathway to OH production at WS ($3.7 \pm 0.6\%$) was overstepped by O_3 photolysis ($13.1 \pm 1.6\%$). This discrepancy was associated with the higher HONO and lower O_3 at TC (Figure S1 and Table 3). As expected, the production rate of OH through HO_2 reacting with NO experienced the most significant increase from $1.4 \pm 0.2 \times 10^7$ molecules $\text{cm}^{-3} \text{ s}^{-1}$ during non-episodes to $3.6 \pm 0.6 \times 10^7$ molecules $\text{cm}^{-3} \text{ s}^{-1}$ during O_3 episodes at WS, which explained more than 90% of the increase of the total OH production. In terms of the losses of OH, reaction between OH and NO_2 was the largest sink of OH at TC. However, OH-initiated oxidations of VOCs consumed most ($52.7 \pm 1.8\%$) of OH at WS. This was reasonable in view of the much more abundant NO_2 at TC than at WS, in contrast to the smaller difference in NMHCs between the two sites (Table 3). Since OH can generally be recycled from the oxidation of VOCs, the lower OH at TC was likely caused by the lower O_3 photolysis and higher consumption of OH by NO_2 , despite the more intensive HONO photolysis. The overall oxidation rate of VOCs by OH was employed to indicate the atmospheric oxidative capacity in previous studies (Elshorbany et al., 2009; Xue et al., 2016). In this study, we found that the oxidation rate of VOCs at TC ($6.1 \pm 2.1 \times 10^6$ molecules $\text{cm}^{-3} \text{ s}^{-1}$ during O_3 episodes and $5.7 \pm 0.9 \times 10^6$ molecules $\text{cm}^{-3} \text{ s}^{-1}$ during non-episodes) was remarkably ($p < 0.05$) lower than that at WS (O_3 episode: $15 \pm 2.5 \times 10^6$ molecules $\text{cm}^{-3} \text{ s}^{-1}$ and non-episode: $8.9 \pm 1.3 \times 10^6$ molecules $\text{cm}^{-3} \text{ s}^{-1}$). The results revealed that the atmospheric oxidative capacity at TC was weaker than at WS for

both O₃ episodes and non-episodes, inconsistent with the findings of Elshorbany et al. (2009) and Xue et al. (2016) who concluded that the atmospheric oxidative capacity was higher in more polluted environments due to the fact that the atmospheric oxidative capacity is positively proportional to the VOCs and OH levels. Both Elshorbany et al. (2009) and Xue et al. (2016) reported very high mixing ratios of VOCs (*e.g.* toluene of 9.5 and 6.3 ppbv, respectively) in the polluted cases, which explained the strong atmospheric oxidative capacity. However, in this study, it is more likely that the higher NO_x at TC consumed more OH and resulted in lower oxidative capacity than at WS, despite the slightly higher VOCs at TC (Table 3).

For HO₂, RO₂ reacting with NO accounted for 56.7±1.1% and 60.7±1.0% of HO₂ production at TC and WS, respectively. Oxidation of CO by OH was also an important pathway leading to HO₂ formation, second to RO₂+NO at both sites. At TC, HO₂ was almost exclusively depleted by NO. However, 10.8±1.8% and 6.5±0.8% of the HO₂ losses were attributable to HO₂-RO₂ and HO₂-HO₂ reactions at WS, respectively, though HO₂+NO was responsible for the most fraction (82.7±2.6%) of HO₂ losses. We believe that the more significant self-consumption of peroxy radicals at WS was closely related to the low NO_x there, which hampered the transfer of oxygen atom from peroxy radicals to NO and further formation of O₃. This was confirmed by the enhanced losses of HO₂ through reactions with HO₂ itself and RO₂ from 3.0±1.2% during O₃ episodes to 24.9±3.4% during non-episodes at WS, because NO_x was more scarce during non-episodes at this site (Table 3). Similarly, in contrast to the negligible influence of RO₂ reacting with HO₂ on RO₂ budget at TC, HO₂-RO₂ reactions played important role in losses of RO₂ at WS, particularly on non-episode days (Figure S7). When OH, HO₂ and RO₂ were summed up, the production and loss rate of RO_x were obtained, as shown in Figure 5(a). Under such circumstance, the transformation and recycling pathways among these radicals can be neglected. For example, OH-initiated oxidation of VOCs consumes OH, which however generates RO₂. Therefore, these reactions were not considered as sources or sinks of RO_x. On one hand, HONO photolysis was the largest source of RO_x at TC (53.7±2.6%), followed by the photolysis of HCHO (21.1±1.6%) and O₃ (18.7±1.5%). However, O₃ photolysis ranked the first among the sources of RO_x at WS with the contribution of 38.6±2.3%, higher than the contributions from HCHO photolysis (34.3±1.4%) and HONO photolysis (18±2.5%). On the other hand, while the reaction between OH and NO₂ served as the sole sink of RO_x at TC, it only explained 50% of RO_x sink at WS with the other half attributable to self-consumption of peroxy radicals.

For details, please refer to Section 3.3.3 (Page 22) and Figure 5 in the revised manuscript and Figure S7 in the revised supplement.

5. It would also be helpful, again in the Supplement, to see ozone, OH, HO₂ and RO₂ concentrations, and ozone and radical rates of formation and loss on a specific episode day. Using averages can lead to a loss of clarity and understanding.

Thanks for the suggestion. The concentrations and formation/loss rates of radicals, *i.e.* OH, HO₂ and RO₂, and O₃ are provided on daily basis in the revised manuscript and revised supplement. More discussions are given for better understanding of the photochemistry.

For details, please refer to the responses to comment #4.

6. Two additional points: O₁D in the caption to Fig 5 should be O¹D. The English needs a good deal of attention, particularly the frequent absence of definite / indefinite articles. Sorry for the mistake in O₁D, which is corrected to O¹D throughout the manuscript. The English, particularly the absence of definite/indefinite articles, has been double checked and revised where necessary.

7. The paper makes a substantial contribution and should be published in ACP. The authors, though, should consider the points made above relating to the overall emphasis of the paper and the clarity of the discussion on chemical processes.

Thanks again for the positive comments on the paper. Revisions are made according to the comments and suggestions, which mainly include the discussions on marine influences and chemical processes at both sites. We hope that the revised manuscript is satisfactory to the referee.

Responses to Referee #2

This paper reports intensive field measurements at two sites over the South China Sea. The spatial distribution of ozone pollution and its favorable synoptic conditions were interpreted. The authors also tried to link, by the sea-land breeze, the transport of continental pollution to oceans and the recirculation of land-originated aged air masses from ocean to the coastal regions. The manuscript is generally well written and easy to follow. The following specific comments should be addressed before it can be considered for publication at ACP.

Specific Comments:

1. Page 1, Line 6: Hong Kong, China.

Thanks for the comment. The author's address has been amended.

2. Page 2, Lines 5-6: the authors may either spell out TC and WS, or just remove them from the abstract.

Thanks for the suggestion. The sampling sites (i.e. TC and WS) have been spelled out.

3. Page 2, Line 15: the word "magnified" may be not appropriate here. The ozone-laden air may be transported to a larger area over the oceans, but should not be "magnified".

Thanks for the Referee's concern. Since this study successfully demonstrates O₃ concentration and production increased at the marine site due to the strong atmospheric oxidative capacity as well as the changed chemical compositions at the reception of continental air, the authors think that the use of "magnified" here is not improper.

4. Page 3, Lines 14-19: to date, the long-term O₃ trend studies were relatively limited in

China. The authors should refer to the following earlier studies in Hong Kong, the PRD region and northern China.

Sun, et al., Significant increase of summertime ozone at Mount Tai in Central Eastern China, *Atmos. Chem. Phys.*, 16, 10637-10650, 2016.

Xue et al., Increasing external effects negate local efforts to control ozone air pollution: a case study of Hong Kong and implications for other Chinese cities, *Environ. Sci. Tech.*, 48, 10769-10775, 2014.

Thanks for providing these references. They have been cited in the revised manuscript.

“However, increasing studies showed that surface O₃ was elevated rapidly in East Asia in the last decade (Ding et al., 2008; Xu et al., 2008; Parrish et al., 2012; **Xue et al., 2014**; Zhang et al., 2014; **Sun et al., 2016**; Lin et al., 2017; Wang et al., 2017a). For example, the observational data revealed that regional O₃ concentrations increased at a rate of 0.86 ppbv yr⁻¹ in Pearl River Delta (PRD) from 2006 to 2011 (Li et al., 2014), at a rate of 0.56 ppbv yr⁻¹ in Hong Kong from 2005 to 2014 (Wang et al., 2017a), **and even at a rate of 1.7-2.1 ppbv yr⁻¹ (summertime only) at Mount Tai in central eastern China (Sun et al., 2016).**”

For details, please refer to page 3, lines 13-20.

5. Page 4, Lines 24-26: a more recent study has investigated the detailed chemical features including the radical chemistry in different air masses arriving at the South China Sea.

Li et al., Oxidizing capacity of the rural atmosphere in Hong Kong, Southern China. *Science of the Total Environment*. 612. 1114-1122. 2018.

Thanks for providing this new reference. Li et al. (2018) has been cited in the revised manuscript.

So far, only a handful of studies deeply evaluated the chemical characteristics of air masses under various synoptic systems (Wang et al., 2005; Guo et al., 2009; Guo et al., 2013; Li et al., 2018).

For details, please refer to Page 4, Lines 26-28.

6. Page 5, Lines 21-22: it is not the case that northeast monsoon prevails in late summer. The O₃ episode occurring in late summer in Hong Kong is mainly related to the tropical cyclones.

Yes, tropical cyclones are one of the principal factors leading to O₃ episodes occurring in late summer and autumn in Hong Kong, which has been acknowledged in the Section 3.2 in the original manuscript. In addition, northeast monsoon prevailing in autumn would also contribute to high O₃ mixing ratio observed in Hong Kong by bringing in high concentrations of O₃ and its precursors from the PRD and other heavy-polluted areas. To make this point clearer, the sentence has been revised and now reads as follows:

High O₃ mixing ratios are frequently observed in Hong Kong in late summer and autumn (Ling et al., 2013) when tropical cyclones and the northeast monsoon prevail, respectively.

For details, please refer to Page 5, Lines 27-28.

7. Page 6, Lines 8-10: it has been known that the traditional commercial NO_x analyzer may be subject to significant positive interference for the NO₂ measurements, especially at the rural and remote areas like WS. The authors need state the uncertainty of the NO₂ measurements and the subsequent observation-based modeling analysis.

Thanks for the comment. The uncertainty of the NO_x measurements has been added in the method section.

It was noteworthy that the measured NO_x might include other oxidized reactive nitrogen that was converted by the molybdenum. Thus, the NO_x concentrations given below

were considered the upper limits of their actual values (Dunlea et al., 2007; Ran et al., 2011).

In addition, the inherent uncertainty of NO_x measurement mentioned above might slightly affect the modeling results.

For details, please refer to Page 6, Lines 12-15 and Page 9, Lines 9-10.

8. Page 8, Lines 16-18: so the OBM was not constrained by the measured HONO and OVOCs, right? This may affect the accurate modeling of OH radicals and ozone formation. As the OVOC measurements were available in the present study, the authors should constrain the model with the measured OVOC data.

Thanks for the comment. The measured OVOCs, as well as the HONO obtained from previously published data, have been used to constrain the OBM. The new results are presented in the revised manuscript. Please see Comment 13 for more details.

9. Page 9, Lines 19-27: it would be better if the authors could provide the time series of model simulations and observations for a direct comparison, maybe in the supporting information.

Thanks for the good suggestion. For comparison, the time series of model simulations and observations have been added in Figure S3 in the revised supplement.



Figure S3. Time series of the WRF-CMAQ simulated and the observed CO and O₃ at WS (left panel) and TC (right panel) during a typical O₃ episode on Oct. 2-4, 2013.

10. Page 10, Table 1: it would be much better if the statistics of the most abundant NHMC and carbonyl species are individually shown, instead of the bulk concentrations.

Thanks for the suggestion. The statistics of the top 10 NHMC and the top 3 carbonyl species are individually shown in Table S5 in the revised supplement.

Table S5. Statistics (Mean \pm 95% C.I.) of the top 10 NMHC and the top 3 carbonyl species observed at TC and WS during O₃ episodes and non-episodes (unit: pptv).

| Compound | TC | | WS | |
|----------|----------------|----------------|----------------|----------------|
| | Episode | Non-episode | Episode | Non-episode |
| Ethane | 2179 \pm 222 | 1852 \pm 256 | 2077 \pm 182 | 1456 \pm 167 |

| | | | | |
|---------------------|----------|----------|----------|----------|
| <i>Propane</i> | 1966±277 | 1572±207 | 1523±126 | 866±126 |
| <i>i-Butane</i> | 1944±371 | 1433±166 | 1559±167 | 810±115 |
| <i>Acetylene</i> | 2083±165 | 1316±145 | 1805±133 | 1086±122 |
| <i>Toluene</i> | 1829±365 | 1357±254 | 1737±388 | 703±183 |
| <i>n-Butane</i> | 1437±163 | 1336±148 | 1160±145 | 480±113 |
| <i>n-Hexane</i> | 733±329 | 1351±443 | 980±299 | 447±121 |
| <i>Ethene</i> | 1140±167 | 1077±171 | 826±99 | 691±94 |
| <i>i-Pentane</i> | 964±145 | 813±123 | 918±99 | 523±96 |
| <i>Benzene</i> | 614±49 | 428±51 | 587±47 | 381±44 |
| <i>Formaldehyde</i> | 5068±454 | 3522±286 | 4257±355 | 2471±180 |
| <i>Acetone</i> | 5064±831 | 3367±445 | 3984±287 | 2086±162 |
| <i>Acetaldehyde</i> | 1807±162 | 1241±115 | 1618±133 | 920±105 |

11. Section 3.2: this section is too long and contains a lot of general description of the typhoon, continental anticyclone, and sea-land breeze (most of them are already well known). The authors may consider to further shorten such general descriptions and mainly highlight the new results obtained in this study.

Thanks for the comment. The Section 3.2 has been further shortened in the revised manuscript by removing some simple descriptive text, for example:

“The main feature of the anticyclones is sinking air at the center with gentle clockwise winds in the northern hemisphere. The air warms up as it sinks by compression leading to warm, cloudless and dry weather, which is conducive to intensive photochemical O₃ formation. In addition, anticyclone is a large-scale weather system which produces long-lasting settled and calm weather for many days or weeks favorable to the accumulation of primary and secondary pollutants.” and

“In general, the temperature difference between the sea and the land is large on the SLB days. Taking 3 Oct. as an example, the maximum hourly temperature at TC was

3.2 °C higher than that at WS during daytime hours, whereas the minimum hourly temperature in the evening was 2.7 °C lower at TC than at WS.”

For details, please refer to Section 3.2 (Pages 14-19) in the revised manuscript.

12. Section 3.3.3: it is not clear whether the modeling analysis was conducted for the campaign average condition or for a particular case. Furthermore, the sub-title of this section may be not appropriate as this section only talked about the simulated OH level and O₃ formation, other than the atmospheric oxidative capacity.

Thanks for the comment. The modeling analysis in section 3.3.3 was conducted for the individual days when VOCs were collected. For the subtitle, we have discussed the atmospheric oxidative capacity in the revised manuscript according to the definition in Elshorbany et al. (2009) and Xue et al. (2016), *i.e.* oxidation rate of VOCs by OH. However, since O₃ production rate is also an important content in this section, the subtitle has been changed to “Atmospheric oxidative capacity and O₃ production rate”.

3.3.3 Atmospheric oxidative capacity and O₃ production rate

O₃ formation is driven by the transformation and recycling of oxidative radicals, including OH, HO₂ and RO₂, collectively referred to as RO_x hereafter. The production and loss rates of these radicals, and their equilibrium concentrations on the canister sampling days were simulated by the PBM-MCM model, as shown in Figure S7.

For details, please refer to Page 22, Lines 20-24.

The overall oxidation rate of VOCs by OH was employed to indicate the atmospheric oxidative capacity in previous studies (Elshorbany et al., 2009; Xue et al., 2016). In this study, we found that the oxidation rate of VOCs at TC ($6.1 \pm 2.1 \times 10^6$ molecules cm⁻³ s⁻¹ during O₃ episodes and $5.7 \pm 0.9 \times 10^6$ molecules cm⁻³ s⁻¹ during non-episodes) was remarkably ($p < 0.05$) lower than that at WS (O₃ episode: $15 \pm 2.5 \times 10^6$ molecules cm⁻³ s⁻¹ and non-episode: $8.9 \pm 1.3 \times 10^6$ molecules cm⁻³ s⁻¹). The results revealed that the atmospheric oxidative capacity at TC was weaker than at WS for both O₃ episodes and non-episodes, inconsistent with the findings of Elshorbany et al. (2009) and Xue et al. (2016) who concluded that the atmospheric oxidative capacity was higher in more

polluted environments due to the fact that the atmospheric oxidative capacity is positively proportional to the VOCs and OH levels. Both Elshorbany et al. (2009) and Xue et al. (2016) reported very high mixing ratios of VOCs (*e.g.* toluene of 9.5 and 6.3 ppbv, respectively) in the polluted cases, which explained the strong atmospheric oxidative capacity. However, in this study, it is more likely that the higher NO_x at TC consumed more OH and resulted in lower oxidative capacity than at WS, despite the slightly higher VOCs at TC (Table 3).

For details, please refer to Page 23, Lines 20-33, and Page 24, lines 1-2.

13. Page 21, Lines 8-10: based on the current analysis, I don't agree that the atmospheric oxidative capacity is stronger at the coastal WS than polluted TC site. HONO photolysis is a very important OH source in polluted areas including the TC site (Xue et al., 2016), which was not included in the present study. So the OH levels should be underestimated at TC. Moreover, the lower OH levels at TC should be due to the fast radical cycling given the more abundant VOCs. I presume that the HO₂ and RO₂ levels at TC should be significantly higher than those at WS.

Xue et al., Oxidative capacity and radical chemistry in the polluted atmosphere of Hong Kong and Pearl River Delta region: analysis of a severe photochemical smog episode. *Atmospheric Chemistry and Physics*. 16. 9891-9903. 2016.

The excellent comment is highly appreciated. Firstly, HONO was indeed not input into the model for simulation of photochemistry in this study, as we did not measure HONO concentrations in the sampling campaign. We agree that the absence of HONO might have an influence on the conclusions about photochemistry at the two sites. Therefore, the average diurnal profiles of HONO observed at TC and a coastal background site (Hok Tsui, HT) in Hong Kong were used to present the average levels of HONO at TC and WS, respectively, for model simulations again.

HONO has been recognized as an important source of OH, influencing O₃ formation significantly (Kleffmann, 2007). Since we did not measure HONO mixing ratios in this study, the average diurnal profiles of HONO observed at TC in autumn 2011 (Xu et al., 2015) and at a coastal background site (Hok Tsui, HT) in southeast Hong Kong in autumn 2012 (Zha, 2015) were applied to the photochemical simulations at TC and WS, respectively. Figure S1 shows the

average diurnal cycles of HONO at TC and HT. The use of the aforementioned diurnal profiles might increase the uncertainty of model simulation. However, we believe that the newly introduced uncertainties could not be too high, because HONO observations at TC and HT were carried out 2 years and 1 year before the sampling campaign of this study, respectively. In addition, HT was comparable to WS in aspects of local emissions (nearly free of anthropogenic emissions), air mass category (mixed continental and marine air) and location (to the south of Hong Kong and on SCS).

For details, please refer to Section 2.3 (Pages 8-9).

However, with the inclusion of HONO, the simulated OH, HO₂ and RO₂ at TC were still lower than those at WS. To keep consistency with previous studies (Elshorbany et al., 2009; Xue et al. 2016), the atmospheric oxidative capacity is defined as the overall oxidation rate of VOCs by OH in the revised manuscript. We found that the atmospheric oxidative capacity was also much higher at WS than at TC, due to the higher OH concentration at WS despite the lower VOC levels. In fact, according to our analyses, the lower OH at TC was more related to the higher NO₂, which served as a scavenger of OH through the formation of HNO₃. The lower HO₂ and RO₂ at TC was possibly resulted from their conversion to OH and RO (HO₂ and OH subsequently), under the condition of sufficient NO. However, the recycled OH could be further removed by reacting with NO₂. As a consequence, OH, HO₂ and RO₂ were progressively consumed, which caused their lower concentrations at TC. This section has been substantially revised as follows.

O₃ formation is driven by the transformation and recycling of oxidative radicals, including OH, HO₂ and RO₂, collectively referred to as RO_x hereafter. The production and loss rates of these radicals, and their equilibrium concentrations on the canister sampling days were simulated by the PBM-MCM model, as shown in Figure S7. We noticed that WS featured significantly higher levels of these oxidative radicals on average ($p < 0.05$). The daytime (7:00-19:00 LT) average OH concentration at TC and WS was $(1.5 \pm 0.4) \times 10^6$ molecules cm⁻³ and $(5.5 \pm 0.9) \times 10^6$ molecules cm⁻³ during O₃ episodes, respectively. Consistently, HO₂ and RO₂ at WS were well above those at TC (Table 3). This pattern was also applicable between the two sites during non-episodes. Furthermore, while the difference in OH concentration became less on non-episode days, the

gaps for peroxy radicals (HO_2 and RO_2) between TC and WS widened, as listed in [Table 3](#). From non-episodes to episodes, OH increased at WS alongside with the decreases of HO_2 and RO_2 , likely indicating more conversion of HO_2 to OH by NO, which is an important pathway leading to O_3 formation. Details about this were shown later.

To explain the inter-site differences of the concentrations of oxidative radicals and the variations between O_3 episodes and non-episodes, [Figure S7](#) also provides the breakdowns of the production and loss rates of OH, HO_2 and RO_2 at TC and WS, separately. Overall, the reaction between HO_2 and NO dominated the production of OH at both sites, with the contribution of $69.4 \pm 2.0\%$ and $81.0 \pm 1.5\%$ at TC and WS, respectively. While the photolysis of HONO ranked the second in the production of OH at TC ($22.2 \pm 2.1\%$), the contribution of this pathway to OH production at WS ($3.7 \pm 0.6\%$) was overstepped by O_3 photolysis ($13.1 \pm 1.6\%$). This discrepancy was associated with the higher HONO and lower O_3 at TC ([Figure S1](#) and [Table 3](#)). As expected, the production rate of OH through HO_2 reacting with NO experienced the most significant increase from $1.4 \pm 0.2 \times 10^7$ molecules $\text{cm}^{-3} \text{ s}^{-1}$ during non-episodes to $3.6 \pm 0.6 \times 10^7$ molecules $\text{cm}^{-3} \text{ s}^{-1}$ during O_3 episodes at WS, which explained more than 90% of the increase of the total OH production. In terms of the losses of OH, reaction between OH and NO_2 was the largest sink of OH at TC. However, OH-initiated oxidations of VOCs consumed most ($52.7 \pm 1.8\%$) of OH at WS. This was reasonable in view of the much more abundant NO_2 at TC than at WS, in contrast to the smaller difference in NMHCs between the two sites ([Table 3](#)). Since OH can generally be recycled from the oxidation of VOCs, the lower OH at TC was likely caused by the lower O_3 photolysis and higher consumption of OH by NO_2 , despite the more intensive HONO photolysis. The overall oxidation rate of VOCs by OH was employed to indicate the atmospheric oxidative capacity in previous studies (Elshorbany et al., 2009; Xue et al., 2016). In this study, we found that the oxidation rate of VOCs at TC ($6.1 \pm 2.1 \times 10^6$ molecules $\text{cm}^{-3} \text{ s}^{-1}$ during O_3 episodes and $5.7 \pm 0.9 \times 10^6$ molecules $\text{cm}^{-3} \text{ s}^{-1}$ during non-episodes) was remarkably ($p < 0.05$) lower than that at WS (O_3 episode: $15 \pm 2.5 \times 10^6$ molecules $\text{cm}^{-3} \text{ s}^{-1}$ and non-episode: $8.9 \pm 1.3 \times 10^6$ molecules $\text{cm}^{-3} \text{ s}^{-1}$). The results revealed that the atmospheric oxidative capacity at TC was weaker than at WS for both O_3 episodes and non-episodes, inconsistent with the findings of Elshorbany et al. (2009) and Xue et al. (2016) who concluded that the atmospheric oxidative capacity was higher in more polluted environments due to the fact that the atmospheric oxidative capacity is positively proportional to the VOCs and OH levels. Both Elshorbany et al. (2009) and Xue et al. (2016)

reported very high mixing ratios of VOCs (*e.g.* toluene of 9.5 and 6.3 ppbv, respectively) in the polluted cases, which explained the strong atmospheric oxidative capacity. However, in this study, it is more likely that the higher NO_x at TC consumed more OH and resulted in lower oxidative capacity than at WS, despite the slightly higher VOCs at TC (Table 3).

For HO₂, RO₂ reacting with NO accounted for 56.7±1.1% and 60.7±1.0% of HO₂ production at TC and WS, respectively. Oxidation of CO by OH was also an important pathway leading to HO₂ formation, second to RO₂+NO at both sites. At TC, HO₂ was almost exclusively depleted by NO. However, 10.8±1.8% and 6.5±0.8% of the HO₂ losses were attributable to HO₂-RO₂ and HO₂-HO₂ reactions at WS, respectively, though HO₂+NO was responsible for the most fraction (82.7±2.6%) of HO₂ losses. We believe that the more significant self-consumption of peroxy radicals at WS was closely related to the low NO_x there, which hampered the transfer of oxygen atom from peroxy radicals to NO and further formation of O₃. This was confirmed by the enhanced losses of HO₂ through reactions with HO₂ itself and RO₂ from 3.0±1.2% during O₃ episodes to 24.9±3.4% during non-episodes at WS, because NO_x was more scarce during non-episodes at this site (Table 3). Similarly, in contrast to the negligible influence of RO₂ reacting with HO₂ on RO₂ budget at TC, HO₂-RO₂ reactions played important role in losses of RO₂ at WS, particularly on non-episode days (Figure S7). When OH, HO₂ and RO₂ were summed up, the production and loss rate of RO_x were obtained, as shown in Figure 5(a). Under such circumstance, the transformation and recycling pathways among these radicals can be neglected. For example, OH initiated oxidation of VOCs consumes OH, which however generates RO₂. Therefore, these reactions were not considered as sources or sinks of RO_x. On one hand, HONO photolysis was the largest source of RO_x at TC (53.7±2.6%), followed by the photolysis of HCHO (21.1±1.6%) and O₃ (18.7±1.5%). However, O₃ photolysis ranked the first among the sources of RO_x at WS with the contribution of 38.6±2.3%, higher than the contributions from HCHO photolysis (34.3±1.4%) and HONO photolysis (18±2.5%). On the other hand, while the reaction between OH and NO₂ served as the sole sink of RO_x at TC, it only explained 50% of RO_x sink at WS with the other half attributable to self-consumption of peroxy radicals.

For details, please refer to Section 3.3.3 in the revised manuscript.

14. Page 21, Lines 15-22: it is surprising that the O₃ production rates at WS were much higher than those at TC, especially on the episode days, given that the NO_x and VOC

levels were much higher at TC than at WS during O₃ episodes. What's the possible reason for this?

Thanks for the comment and question. With the addition of HONO in O₃ simulation, the new modeling results show that the net O₃ production rate at WS was comparable to that at TC during non-episodes. However, it was much higher than that at TC during O₃ episodes, due to the more abundant peroxy radicals (RO₂ and HO₂) at WS, in addition to the increased NO during O₃ episodes which unleashed the potential of O₃ production through the reactions between peroxy radicals and NO. It should be noted that the increase of NO at WS during O₃ episodes did not lead to O₃ reduction, unlike the situation in most urban environments including TC, because O₃ formation at WS was limited by both VOCs and NO_x and more sensitive to NO_x without the input of continental air. Overall, despite the lower VOCs and NO_x, the concentrations of peroxy radicals at WS were higher than at TC (the reasons have been discussed in responses to comment #13), and the increase of NO during O₃ episodes accelerated O₃ formation through the reactions between peroxy radicals and NO.

Furthermore, the production and loss rates of O₃ were simulated (Figure 5(b)). Despite the increased O₃ mixing ratio during episodes (Table 3), there was no significant change in net O₃ production between O₃ episodes (2.5 ± 1.0 ppbv/h) and non-episodes (2.5 ± 0.5 ppbv/h) at TC ($p > 0.05$), suggesting that regional transport might play critical roles in regulating O₃ levels at TC. In fact, previous studies (Huang et al., 2006; Jiang et al., 2008) have repeatedly confirmed that O₃ pollution at this site could be aggravated under northerly winds and/or downdraft on the periphery of typhoon. In contrast, the net O₃ production increased remarkably from non-episodes (2.8 ± 0.5 ppbv/h) to O₃ episodes (6.6 ± 1.1 ppbv/h) at WS. Obviously, O₃ production at WS was much higher than at TC during O₃ episodes, while they were comparable during non-episodes. This was likely due to the more abundant peroxy radicals (RO₂ and HO₂) at WS than at TC, in addition to the increased NO_x during O₃ episodes which enhanced the reactions between the peroxy radicals and NO (increasing O₃ formation). Insight into the O₃ production pathways found that the reaction rates of RO₂+NO and HO₂+NO were significantly enhanced from 1.6 ± 0.2 and 2.0 ± 0.4 ppbv/h during non-episodes to 3.2 ± 0.5 and 5.2 ± 0.9 ppbv/h during O₃ episodes, respectively. Our recent study (Wang et al., 2017b) revealed that O₃ formation at WS was in a

transition regime and much more sensitive to NO_x during non-episodes, when O_3 production through peroxy radicals reacting with NO was seriously limited by the low NO_x . During O_3 episodes, with the increase O_3 precursors (particularly NO_x), these reactions were accelerated and the net O_3 production increased substantially. Detailed discussion on the O_3 photochemistry at WS can be found in our recent publication (Wang et al., 2017b).

For details, please refer to Section 3.3.3 in the revised manuscript.

15. Section 3.3.3 and Figure 5: it would be better if the ozone production rates were expressed in ppb/h so that it can be easily compared with the observed ozone increase.

The good suggestion has been accepted with thanks.