Anonymous Referee #1

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The authors present the photochemical oxidation processes simulated by a chemical box model with constraints of field measurement data in four Chinese megacities. The ROx radical budget, OH reactivity, ozone production, and particulate nitrate formation are assessed. The results provide some insights into the formation of secondary pollution such as ozone and nitrate, which are helpful for formulating the air pollution control policy in the polluted regions of China. Hence, this manuscript can be considered for publication after the following comments being properly addressed.

Answer:

We thank the comments and suggestions from the reviewers, which help to improve the manuscript considerably. The response and changes are listed below.

Major Concerns:

A major concern is on the representativeness of measurement results given their relatively short periods, i.e. 1-2 weeks in each city. Are the measured conditions of ozone pollution and ozone precursors typical for the individual cities? Can these results reflect the difference in the photochemical pollution condition and chemical environment among these cities, e.g., less serious pollution in Chongqing? A comment on this would be helpful.

Answer:

We compared the measurement presented in this study to the observation obtained by the environmental monitor stations. The Chinese EPA station data of the same year are derived. We added figures of the EPA station results in four cities in the supplement (Fig. S5). In general, the O₃ concentrations presented in this study are comparable to the maximum of monthly averaged O₃ concentrations derived from the EPA monitor station data for the same year. As shown in Fig. S5, the O₃ concentrations are in general lower in Chongqing than those observed in the other three cities.
Figure S5. The monthly averaged diurnal profiles of measured O$_x$, O$_3$, NO$_2$, CO, PM2.5 concentrations in (a) Beijing, (b) Shanghai, (c) Guangzhou, and (d) Chongqing.

We added sentences in Line 23 Page 4”Given the relatively short periods for these campaigns, one concern is about the representativeness of measurements. We compared the observation
from these intensive campaigns to the routine measurement obtained in the environmental monitor stations operated by the Chinese environmental protection agency (Fig. S5). We found that the mean diurnal profiles of \( \text{O}_3 \) and \( \text{O}_x \) obtained in all sites are comparable to the highest monthly averaged diurnal profiles for the same city (bias < 20%). The relatively small \( \text{O}_3 \) and \( \text{O}_x \) concentrations observed in Chongqing compared to other cities (Fig. 2) is consistent with the environmental monitor stations observation (Fig. S5). Therefore, it suggests that the ozone pollution is less severe in Chongqing compared to the megacities in eastern China.”

Another concern is on the lack of direct measurements of some key radical precursors, such as HONO and carbonyls. This would influence the modeling results of radical budget as well as ozone and nitrate formation. In this study, the authors scaled the HONO concentrations to 0.02*NO\(_2\), and performed sensitivity run by turning off the scaling. But the key question here is if the scaling factor of 0.02 is appropriate. What are the scaled HONO levels in the model for the four cities? Using a different scale factor may change the budget of primary RO\(_x\) sources and OH levels. The authors are recommended to perform more sensitivity tests with different scale factors and comment on its influence on the major conclusions of this study.

**Answer:**
Although the HONO to NO\(_2\) ratio is relative robust and constant as reported in other field campaigns (Elshorbany et al., 2012), such simple parameterization could increase the uncertainty of our model calculation. We performed more sensitivity tests to demonstrate the uncertainty for this simple parameterization and found the model results are not so sensitive to the parameterization (Fig. S8). We added a discussion in Line 24 Page 7 “Although the HONO to NO\(_2\) ratio is relative robust and constant as reported in other field campaigns (Elshorbany et al., 2012), such simple parameterization could increase the uncertainty of our model calculation. To further investigate the uncertainty from this simple parameterization, the scaling factor is varied from 0.15 to 0.3. The modelled OH concentrations change by less than 10% if the HONO scaling factors change by 50% (Fig. S8). Besides, the modelled HO\(_2\)
and RO₂ concentrations are relatively stable with different HONO scaling factors. The different scaling factors also have impact on the model generated species, e.g. HCHO (Table S4). In fact, the higher HONO concentrations lead to more active photochemical reactions and more HCHO production. The higher HCHO concentrations could further enhance the photochemistry by more radical photolytic sources in return. Therefore, the higher (lower) modelled radical concentrations due to increase (reduce) the HONO scaling factors are also affected by the corresponding change in modelled HCHO concentrations. This demonstrates the nonlinearity of the photochemical system. Nevertheless, the parameterized HONO concentrations are in the range of 0.3 to 0.6 ppbv during daytime (Table S4), which are consistent with previous in-situ measurements in urban areas (Lu et al., 2013; Li et al., 2010; Ren et al., 2003; Kanaya et al., 2007). To evaluate the impact of missing HONO source on the radical chemistry, we switched off the scaling between HONO and NOₓ in a sensitivity test (Fig. S8). Therefore, the results show that OH concentrations reduce by about 20% if the only homogenous source is considered. The modeled HO₂ and RO₂ concentrations are also reduced by 15-20% (Table S4)."
Moreover, how are the carbonyls treated within the model? What are the measured or simulated levels of major carbonyls such as formaldehyde, etc.?

Answer:

We added the discussion on the OVOC in Line 39 Page 5 “The OVOCs concentrations are simulated by the box model. The modelled HCHO concentrations are in the range of 3 to 8 ppbv (Fig. S7), which are consistent with the previous studies in these regions (Zhang et al., 2012; Song et al., 2018; Chen et al., 2016; Tang et al., 2009). The modelled acetaldehyde concentrations are in the range of 2 to 3 ppbv in Beijing, Shanghai, and Chongqing but 1 ppbv
larger in Guangzhou because the larger contribution of aromatics VOCs which produce acetaldehyde from their OH degradation.”

![Graph showing mean diurnal profiles of formaldehyde (HCHO), acetaldehyde (ACD), and peroxycetyl nitrate (PAN) concentrations in four cities.]

Figure S7. The mean diurnal profiles of modelled formaldehyde (HCHO), acetaldehyde (ACD) and peroxycetyl nitrate (PAN) concentrations in four cities.

Section 3.1: a detailed discussion on the concentrations and speciation of VOCs in the four cities are needed. It is much helpful for the readers to understand the different chemical mix in these cities and to better judge the following modeling results. A table summarizing the measured VOC species and related parameters would be good.

Answer:

We added a table showing top 10 $k_{OH}$ contributing VOCs in Table 2 and a table showing all measured VOC and their concentrations in supplement (Table S3). The mean diurnal profiles of top 10 VOC are added in supplement (Figure S6).

Table S3 Summary of measured and modelled species
<table>
<thead>
<tr>
<th>Species</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Measured</strong></td>
<td>T, P, RH, photolysis rate, NO, NO₂, O₃, C₂-C₈ alkanes, C₂-C₆ alkenes, C₆-C₁₀ aromatics</td>
</tr>
<tr>
<td><strong>Modelled</strong></td>
<td>OH, HO₂, RO₂, k₀H, OVOCs (including formaldehyde, acetaldehyde, methacrolein, other aldehydes, glyoxal, acetones, methyl vinyl ketone, other ketones, methanol, ethanol, phenol, formic acid, acetic acid and higher acids, and so on)</td>
</tr>
<tr>
<td><strong>Scaled</strong></td>
<td>HONO (=0.02×NO₂)</td>
</tr>
</tbody>
</table>

Figure S6. The mean diurnal profiles of top 10 $k_{OH}$ contributing VOCs concentrations in Beijing, Shanghai, Guangzhou, and Chongqing.

We move the discussion of VOC speciation to section 4.1. We added a discussion on the concentrations and speciation of VOCs in the four cities in the end of the section “The top 10
OH reactivity contributing VOCs are summarized in Table 2. The order of VOCs is sorted by the averaged OH reactivity for four cities. Among all, propene are the most important OH reactivity contributor, which contributed about 0.4–0.6 s\(^{-1}\) (Table 2). The small VOCs (propene, ethane, ethene) are relatively important with respect to OH reactivity. 9 out of the top 10 VOCs are alkenes and aromatics (except ethane). In Guangzhou, the xylene (m,p-, and o-) and toluene are also important OH reactants, consistent with the inventory study (Zheng et al., 2009). The diurnal profiles are shown in Fig. S6. The observed anthropogenic VOC concentrations show typical diurnal profile that increase during night and decrease during afternoon. One exception is Shanghai site, the mean diurnal profiles of propene and 1,2,4-trimethybenzene are flat, while that of styrene shows peak around noontime, indicating unique VOC emission feature in that site.

The OVOCs concentrations are simulated by the box model. The modelled HCHO concentrations are in the range of 3 to 8 ppbv (Fig. S7), which are consistent with the previous studies in these regions (Zhang et al., 2012; Song et al., 2018; Chen et al., 2016; Tang et al., 2009). The modelled acetaldehyde concentrations are in the range of 2 to 3 ppbv in Beijing, Shanghai, and Chongqing but 1 ppbv larger in Guangzhou because the larger contribution of aromatics VOCs which produce acetaldehyde from their OH degradation."

Section 3.3.2 and Figures 7-8: it is interesting that ozonolysis reaction of VOCs is identified as a significant daytime source of ROx radicals in four cities. This source is usually considered to be not important at daytime as it only occurs for unsaturated VOCs which are generally at low concentration levels at daytime. So what are the major VOC species contributing to this radical source, and what are their concentration levels in these four cities? In addition, some studies found photolysis of OVOCs is an important radical source. However, its contributions estimated in this study were quite small (3-6%) in all four cities, and the production rates of RO2 radicals (P(RO2); 0.2-0.3 ppb/h) were also much smaller compared to the other studies. These results are a little bit strange, and the authors may need examine what OVOC species are considered in the model. More discussions of the radical budget analysis are needed.
As shown in the newly added Table 2, 5 out of the top 10 VOC could react with O₃ to produce ROx radicals. However, the reaction rates with O₃ and with OH are different for different alkenes. We added a discussion in Line 3 Page 7 “The ozonolysis reactions mainly contributed by trans-2-butene in Beijing (55%), Guangzhou (42%), and Chongqing (39%), whose concentrations are in the range between 0.1 to 0.3 ppbv (Fig. S6). Although trans-2-butene is only the 8th important VOCs with respect to OH reaction (Table 2), it become the most important O₃ reactants producing ROx radicals due to its fast reaction rate with O₃ (1.9×10⁻¹⁶ cm³s⁻¹ compared to 1.0×10⁻¹⁷ cm³s⁻¹ of propene, rate constant derived from MCM3.3.1 [http://mcm.leeds.ac.uk/MCMv3.3.1/home.htm]). In Shanghai, propene becomes the most important alkene with respect to O₃ reaction, which accounts for about 42% of the total alkene ozonolysis reactions. Actually, the relatively high contribution from alkene ozonolysis to the ROx radical primary sources could be one of the important characteristics for ROx radical primary sources in Chinese megacity. The importance of alkene ozonolysis was also found in Santiago, Chile (Elshorbany et al., 2009) and Essex, UK (Emmerson et al., 2007), where alkene ozonolysis contributed about 20% to the total radical primary production.”

The role of OVOCs (except HCHO) photolysis are highly variable from literatures, which demonstrates the fate OVOCs highly depends on chemical conditions. We added a discussion on the role of OVOC photolysis to radical chemistry to replace the sentences from Line 28 to Line 33 Page 7 “The RO₂ primary source strength is in the range of 0.2 to 0.3 ppbv/h, which is mainly contributed by alkene ozonolysis and OVOC photolysis (Fig. 8). In this study, the OVOC photolysis mainly includes carbonyl-containing compounds (e.g. acetaldehyde, aldehydes with carbon numbers larger than 3), which are generated by the box model. The modelled acetaldehyde concentrations are in the range of 2 to 4 ppbv (Fig. S7), consistent to the observations in Beijing (Chen et al., 2016) and Hong Kong (Lyu et al., 2016). The photolysis rate of carbonyl-containing compounds (except HCHO) is about one third to a quarter of the HCHO photolysis rate. In comparison, this ratio could be close to or even higher than 1 in other urban studies (Ren et al., 2013; Volkamer et al., 2010; Emmerson et al., 2007; Michoud et al., 2012; Whalley et al., 2018; Xue et al., 2016). In contrast, the relatively
small contribution from other carbonyl-containing compounds photolysis than HCHO photolysis were reported in an urban and suburban site in Hong Kong (Lyu et al., 2016), where the acetaldehyde concentrations were about 1 to 2 ppbv, comparable to our model simulation. Such large discrepancy in the role of other OVOC photolysis to the radical production highlights the importance to measure these radical precursors in the future studies.”

Specific Comments:

Title: Atmospheric oxidation capacity in four Chinese megacities

Answer:

We changed the title to be “Daytime atmospheric oxidation capacity in four Chinese megacities during photochemical polluted season: a case study based on box model simulation”.

Page 1, Line 40: is one of the major threats

Answer:

Corrected.

P2, L1-2: it would be better to introduce Chongqing here after introducing the other three megacities

Answer:

We moved the introduction of Chongqing in Line 3 Page 2 “The Chengdu-Chongqing city group (population 90 million) locates in Sichuan Basin (SCB), southwest of China, representing the developing city clusters. Chongqing is the biggest city in the southwest of China, which suffers from severe air pollution as well.”

We moved the sentence “Although the new city clusters also suffer from air pollution, only sparse researches have been conducted in these regions, especially for the secondary pollution formation. For the SCB region, only limited studies have been performed regarding the oxidation capacity. Chengdu is evaluated using an observational-based model which found similar radical concentration and ozone production rate (Tan et al., 2018). The VOC and
ozone formation is evaluated in Chongqing (Su et al., 2018; Li et al., 2018).” to Line 23 Page 2.

**P2, L4: have declined characterized by high concentrations of ozone and fine particles**  
**Answer:**  
We changed the sentence to be “As a result, the primary pollutant concentrations have declined since then. However, secondary pollution characterized by high concentrations of ozone and fine particle has become the major contributor to air pollution.”

**P2, L11: the role of**  
**Answer:**  
Corrected.

**P3, L7: are located**  
**Answer:**  
Corrected.

**P3, L16: according to Table 1, the measurement in Beijing was in July, not in June.**  
**Answer:**  
Corrected.

**P3, L21: Instrumentation**  
**Answer:**  
Corrected.

**Section 2.2: a table summarizing all of the measurement species (especially the VOC species) and techniques is needed, maybe in the supplement, for better understanding the present study.**  
**Answer:**  
We added a table to describe the instrumentation in the supplement (Table S1). The measured
VOCs listed are presented in Table S3.

P3, L29-30: rephrase this sentence.

Answer:
We changed the sentence to be “A box model based on the Regional Atmospheric Chemical Mechanism version 2 (Goliff et al., 2013) is used to simulate the concentrations of the OH, HO₂ and RO₂ radicals concentrations and other unmeasured secondary species concentrations.”

P4, L5: AHC is used here but AVOCs is used later. Keep them consistent and spell out them at their first appearance.

Answer:
We changed all AHC to AVOC. For consistency, we changed NHC to NVOC.

P5, L1-8: it seems that the discussion in this paragraph is not relevant here

Answer:
We moved the paragraph to Line 13 Page 5.

P6, L4-5, “The maximum of OH”: rephrase this sentence.

Answer:
We changed the sentence to be “The peak of OH mean diurnal profile is highest in Beijing and Shanghai (7×10⁶ cm⁻³).”

P6, L13-14, “the larger correlation slope”: rephrase this sentence since solar radiation cannot directly converts to radicals

Answer:
This sentence is only a qualitative description and not related to the content. Hence, we removed this sentence.

P9, L33-34: a brief discussion of the NHC levels would be much helpful here.
We added a sentence in Line 34 Page 9 “The only component of NVOC is isoprene, which are on average 0.3 ppbv in Beijing, 0.1 ppbv in Guangzhou, and 0.4 ppbv in Chongqing, but reduce to negligible in Shanghai (below detection limit, Table S3).”

P9, L35-36: “reducing NOx could lead to increase in Ox concentrations” is not absolutely correct. There is a threshold below which the NOx emissions were reduced to, the ozone would be significantly decreased.

Answer:
We changed the sentence to be “For NOx, the RIR values are negative indicating the ozone production is in NOx-titration regime. A slight reduction of NOx could lead to increase in Ox concentrations within the NOx-titration regime.”

P10, L6, “In another word, if HONO is”: uncomplete sentence.

Answer:
The sentence should be “The reduction of radical termination by OH+NO2 reaction compensates the reduction of radical primary source due to HONO photolysis. Therefore, a larger negative effect shows up in the RIR analysis in the sensitivity test (Fig. S6).”

P10, L34: change decomposition to deposition

Answer:
Changed.

Section 4.2: is the nocturnal nitrate formation from the N2O5-related processes taken into account in the present analysis?

Answer:
Only daytime processes is considered in this study. I added a sentence to state it in Line 5 Page 11 “One should note that the nitration formation from N2O5 hydrolysis is not taken into account in this study, which could lead to negative bias in the nitrate production.”
P12, L25: change Shang to Shanghai

Answer:

Corrected.

Figure 2: Anthropogenic Volatile Organic Compounds (AHC): keep consistent.

Answer:

We changed all AHC to AVOC.

Figure 3: Chengdu should be Chongqing? In addition, what does “model” mean in the figure legend?

Answer:

We changed the caption to be “Figure 3. Mean diurnal profile of contributions from all measured species for OH reactivity in Beijing, Shanghai, Guangzhou, and Chongqing. The filled areas represent different atmospheric constituents. The model denotes the sum of model generated species such as formaldehyde, acetaldehyde.”

Figure 6: what does “variability” stand for?

Answer:

We changed the caption to be “The vertical bars denote the daily variability of model calculated radical concentrations.”
Reference:


Li, G., Lei, W., Zavala, M., Volkamer, R., Dusanter, S., Stevens, P., and Molina, L. T.: Impacts of HONO sources on the photochemistry in Mexico City during the MCMA-2006/MILAGO Campaign, Atmospheric Chemistry and Physics, 10, 6551-6567, 10.5194/acp-10-6551-2010, 2010.


