The manuscript entitled “Insights into the abnormal increase of ozone during COVID-19 in a typical urban city of China” by Kun Zhang et al. explored the drivers of elevated ozone concentration during COVID-19 lockdown. The manuscript provides valuable information for understanding ozone chemistry under rigorous emission reduction measures and efficiently directing ozone mitigation in the future. I would recommend publication if my following concerns are well addressed.

Response: We thank the reviewer for the positive and constructive comments and suggestions. All concerns have been carefully addressed. Below is our point-by-point response to each comment, marked in blue. Changes made to the main text are presented in green.

General comments:

(1) VOCs were measured by a PTR-TOF-MS in this study. However, this method cannot measure alkane and most alkene species, which will underestimate the ozone production and could mislead the diagnosis of ozone sensitivity regimes. Therefore, some uncertainty analysis regarding this deficiency is necessary.

Reply: Thanks for the constructive comment. Yes, the VOCs measured by PTR-TOF-MS do not include C2~C5 alkenes and alkanes. Unfortunately, we do not have traditional VOC observations during this period. To understand the possible underestimation of ozone production due to limitations of the measurement, we collected the observational data of C2~C5 alkenes and alkanes during the autumn of 2018 at the same site. We further performed simulations by including assumed diurnal variation of ethene, propene, butene, ethane, propane and butane which are key C2~C5 alkenes and alkanes at this site, in the model. During different runs, we added 0.5*[alkenes], 1*[alkenes], 1.5*[alkenes], or 2*[alkenes] in the model and calculate the uncertainties caused by alkenes. As shown in Figure 1 below, deficiency of C2~C5 alkenes and alkanes can lead to underestimation of O_3 during daytime. On average, adding 0.5~2 times alkenes or alkanes could lead to 1.65%~9.49% or 1.37~5.36% increase of simulated O_3, respectively. Although the deficiency of C2~C5 alkenes and alkanes could bring in some uncertainty, the results of base case are still reliable for further analysis. Relevant description has been added in the revised manuscript, please refer to Page 22, Line 422-435:

Due to limitations in the observations, several issues should be noted in the application of the OBM model to evaluate the local chemistry in the present study. Firstly, deficiency of the observation of C2~C5 alkenes and alkanes could lead to underestimation of the simulated O_3. To understand the possible underestimation of ozone production due to limitations of the measurement, we collected the observational data of C2~C5 alkenes and alkanes during the autumn of 2018 at the same site. To analyze the uncertainties, we further performed simulations by including assumed diurnal variation of ethene, propene, butene, ethane, propane and butane which are key C2~C5 alkenes and alkanes at this site, in the model. On average, adding 0.5~2 times alkenes or alkanes could lead to 1.65%~9.49% or 1.37~5.36% increase of simulated O_3, respectively (Figure S7 and S8). In addition, the deficiency of C2~C5 has potential to cause uncertainty in O_3 formation potential. To quantify this impact, the EKMA analysis with the hypothetical diurnal variation of C2~C5 was also performed. The results suggested that the influence of the deficiency of C2~C5 alkenes and alkanes on the O_3 formation sensitivity is negligible (Figure S9). Therefore, although the deficiency of C2~C5 alkenes and alkanes could bring in some uncertainty, the results of base case are still reliable for further analysis.

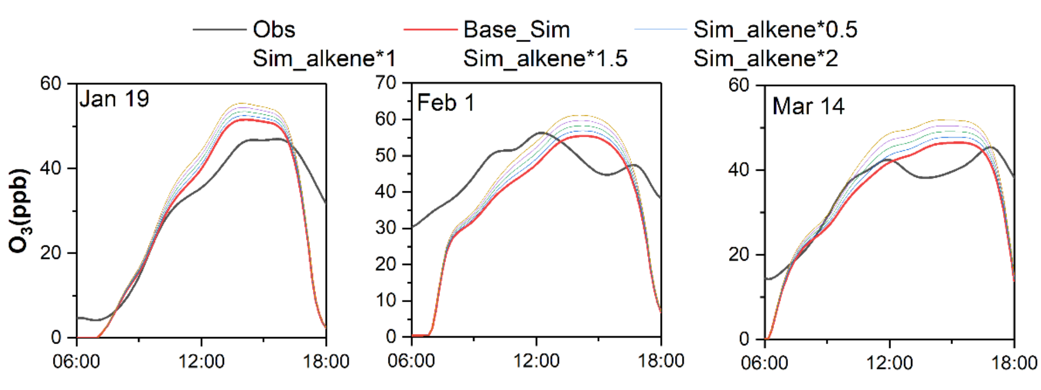

Figure 1 Sensitivity analysis of the influence of alkenes

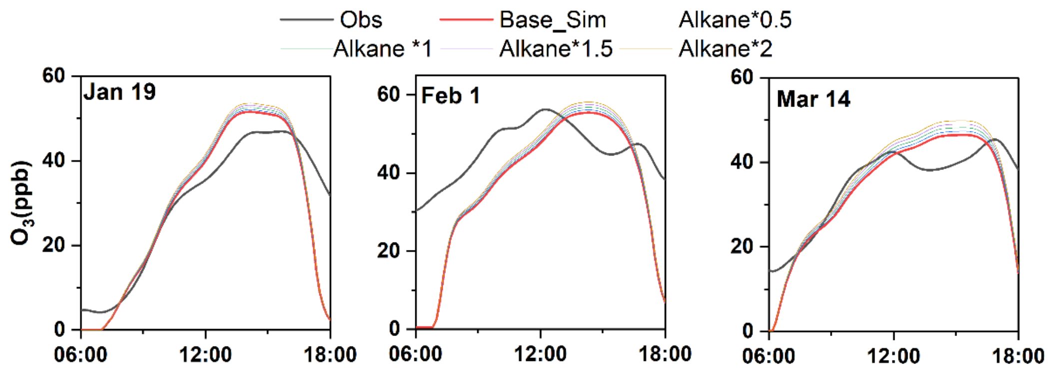

Figure 2 Sensitivity analysis of the influence of alkanes

(2) Temperature and solar radiation increase rapidly from Pre-lockdown period to Full-lockdown period, which could significantly contribute to the increase in ozone concentration during Full-lockdown period. This influence is not fully considered in the manuscript. Relevant analysis is also suggested to be included.

Response: Thanks for the comment. According to Figure 3 in the revised manuscript, the discrepancy between the $O_{3,Obs}$ during Pre-lockdown and Full-lockdown period could be partially attributed to changes of meteorological condition (11.74 ppb). Apart from the influence of meteorological condition, the $O_{3,Normal}$ in Full-lockdown period is still 0.64 ppb higher than that during Pre-lockdown period, which could only be attributed to the changes in emissions between the two periods. Relevant descriptions have been inserted to the revised manuscript, please refer to Page 10, Line 215-224:

It is obvious that the $O_{3,Obs}$ during Pre-lockdown period is much lower than that during Full-lockdown period in both years, which is partially attributed to the negative influence of meteorological conditions during Pre-lockdown period (Figure 3). This is consistent with the increasing temperature and solar radiation, which could significantly contribute to the increase of ozone concentration, from Pre-lockdown to Full-lockdown period. It should be noted that meteorology constrained O_3 concentrations by 3.9 ppbv during the Full-lock down period in 2019. Apart from the influence of meteorological condition, the $O_{3,Normal}$ in Full-lockdown period in 2020 is still 1.46 ppbv and 0.64 ppb higher than that during Full-lockdown period in 2019 and that during Pre-lockdown period in 2020, indicating that improper decline of precursor emissions was possibly the key reason for the obvious increase of O_3 during Full-lockdown period in 2020.

Specific comments:

Line 28: “the observed O_3 “should be changed into “the increase in the observed O_3”.

Response: We have revised this sentence as suggested.

Line 34-35: Here, the authors describe that the changes in precursor emissions (or NO_x/VOCs ratio) contributed 2.4 ppbv to the O_3 increase, which is inconsistent with 5.1 ppb in lines 27-28. Please double check it.

Response: We are sorry for the improper description. We used deweathered method and box model to estimate the influence of emission changes, respectively. The result from deweathered method was described in Line 27-29, while the result from box model was shown in Line 34-35. To avoid misdirection, we have revised Line 34-35 into:

Additionally, box model results suggested that the decrease in NOx/VOCs ratio during Full-lockdown period was supposed to increase the MeanO_3 by 2.4 ppbv.

Line 58-59: also include actinic flux in meteorological conditions and cite the papers (1, 2).

Response: We have included actinic flux in meteorological conditions and cited the papers as suggested.

References:

Wang et al., The impact of aerosols on photolysis frequencies and ozone production in Beijing during the 4-year period 2012–2015. Atmos. Chem. Phys. 19, 9413-9429 (2019).

Wang et al., Exploring the drivers of the increased ozone production in Beijing in summertime during 2005–2016. Atmos. Chem. and Phys. 20, 15617-15633 (2020).

Line 175-176: The influence of RH on ozone is very complicated. Higher humidity is conducive to OH production and thus likely increase O_3 production. I suggest to add some references about RH influence here and simulate the influence of RH on ozone by box model.

Response: We agree that the influence of RH on O_3 is complicated, which are non-linearly related. We have added some references about RH influence. In addition, we have added sensitivity analysis to quantify the influence of RH by increasing or decreasing RH by 10%, and the results are exhibited in Figure 3. On average, reducing RH by 10% leads to 0.28% increase of the simulated O_3, and this influence dropped to -0.35% when RH was 5% lower than the base case. When increasing RH by 5% or 10%, positive influence on the simulated O_3 was found. Therefore, we have revised the descriptions in the manuscript, please refer to Page 9, Line 198-201:

The relatively higher T was in favor of O_3 formation during the Full-lockdown period in 2020. As for RH, the influence on O_3 is nonlinear (Zhang et al., 2020), and based on our sensitivity test, lower RH could lead to decrease or increase of O3 concentration (Figure S2).

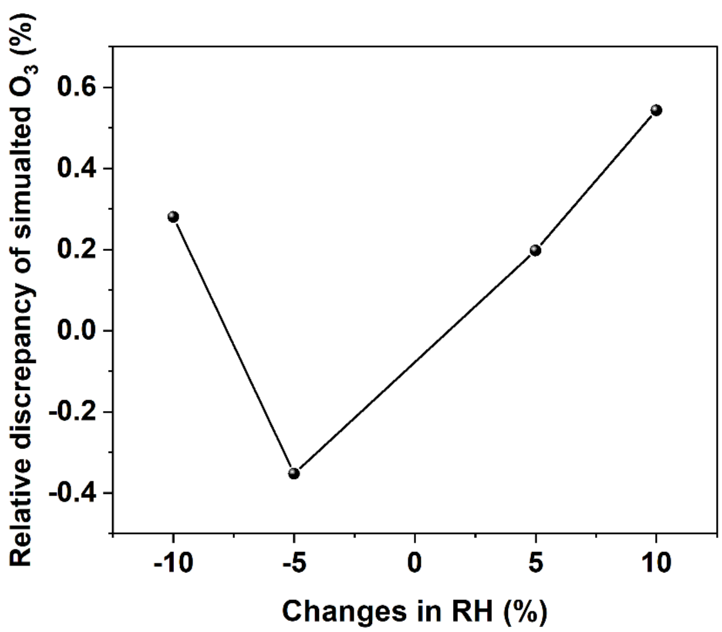

Figure 3. Sensitivity analysis of the influence of RH

Line 177: please explain why RH>70% can be an indicator of adverse weather conditions.

Response: We are sorry for this misleading information, RH>70% is not an indicator of adverse weather conditions. Therefore, relative description has been removed.

Line 192: What does the r^2 represent? You should state out it in Section 2.4.

Response: The R^2 represents the determining coefficient of the model and a R^2 close to 1 means the model can reproduce the observation well. We have stated out R^2 in section 2.4. Please refer to Line 160-162:

The results suggest that the highest coefficient of determination (R^2, 0.84) was obtained when ntree, nsample and minimal node size was set as 300, 300, and 5, respectively (Table S1 and S2).

Line 195: I think "$O_{3,Obs}$" should be "$O_{3,Normal}$" here.

Response: Thanks for pointing this out. Yes this should be "$O_{3,Normal}$". We have revised it in the latest version of manuscript.

Figure 3 and Figure 12: In figure 3, $O_{3,Normal}$ during Full-lockdown period is higher than that during Pre-lockdown period by 12 ppb. However, the corresponding value is only 2.4 ppb. Please explain this inconsistency.

Response: We apologize for the mistake in the original figure 3, which used the predicted O_3 instead of the weather-normalized O_3 data. We have updated figure 3 with the correct result, and the figure shows the $O_{3,Normal}$ during Full-lockdown is 0.7 ppbv higher than that during Pre-lockdown period, which is close to the value in figure 12 (2.4 ppb).

Figure 3: My understanding is that the deweathered method normalizes the influence of meteorological factors on the difference between the same periods in different years. Were meteorological factors between different periods also normalized? The authors should clearly explain this in Section 2.4. This is important to figure out the influence of meteorological factors on ozone increase during Full-lockdown period compared to pre-lockdown period.

Response: The meteorological factors between different periods were not normalized. They were sampled to predict concentrations many times (and aggregated) to calculate the normalized time series. The corresponding description has been revised in Section 2.4. Please refer to Line 164-169:

Training of the models was conducted on 80% of the input data and the other 20% was withheld from training. To avoid the disadvantage of overfitting during the training of RF, a process called bagging (or bootstrap aggregation) was adopted. Bagging results in new, sampled set called out-of-bag (OOB) data. A decision tree is then grown on the OOB data. Therefore, all the decision trees are grown on different observations and avoid the overfitting (Grange and David (2019)).

Line 214-215: I suggest to at least give some evidences that the decrease in VOC is due to the decrease in industrial activities and traffic volume. Besides industrial activities and traffic volume, solvent usage is also an important source of VOC.

Response: Thanks for the helpful suggestion. We summarized the electricity consumption of key industries in Changzhou during our observation, and calculated the corresponding VOC emissions using the following equation. We also collected the traffic volume data during the observational period.

$$E_o = \sum_{i=1}^{n} \frac{E_{pi}}{S_{pi}} \times S_{oi}$$

where E_o (unit: t) is the total daily VOC emission from industrial sources during the observation; E_{pi} (unit: t) and S_{pi} is the daily VOC emissions and electricity consumption of the ith industry during the second national pollution census, respectively; S_{oi} is the daily electricity consumption during our observation; n is the number of industries. The VOC emissions data and the electricity consumption data was obtained from the second national pollution census and Atmospheric Information Platform of Changzhou (http://58.216.50.59/), respectively. It is clearly shown that the time series of industrial VOC emissions and traffic volume showed similar trend during the observation, suggesting that the lock-down policy strongly influence industry and traffic simultaneously. In addition, area source like solvent usage is also an important source of VOCs, which is prohibited during the Lock-down period. To prove that the decrease of VOCs during Full-lockdown period is caused by changes in human activities (industries, traffic, and solvent use, etc) the variation of typical industry-derived VOC (styrene) and traffic/industry-derived VOC (benzene toluene and xylene) are presented in Figure 4. In addition, the relevant description has been added in the revised manuscript, please refer to Page 11, Line 235-236:

This is proved by the trend of traffic volume, VOCs emission and traffic/industrial-derived VOCs (Text S1 and Figure S3).

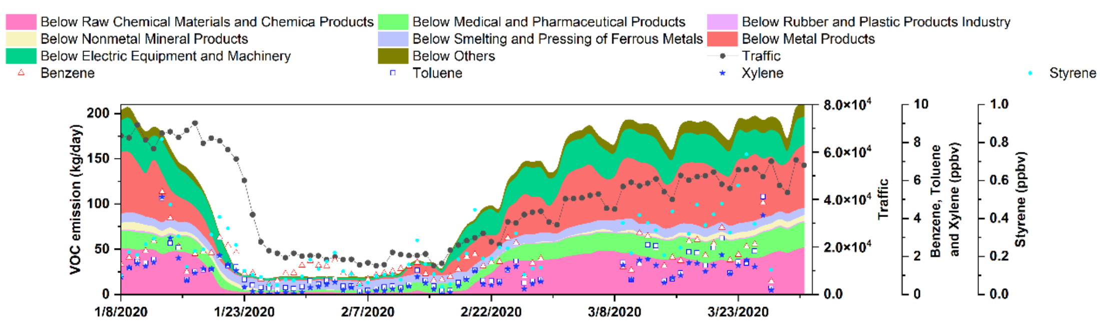

Figure 4 Time series of industrial-derived VOCs emissions, traffic volume, and key VOC tracers.

Line 266-268: The expression is ambiguous here. Acetaldehyde and formaldehyde don't belong to aromatics.

Response: We are sorry for this mistake. Text has been revised:

Among VOCs, xylene exhibited the maximum OFP value (68.6 ± 59.3 μg/m^3), followed by acetaldehyde (28.8 ± 6.4 μg/m^3), toluene (25.7 ± 20.1 μg/m^3) trimethylbenzene (25.4 ± 15.8 μg/m^3), and formaldehyde (22.7 ± 9.1 μg/m^3).

Line 273-274: "As for alkene, this could be explained by their chemical reactivities, which led to the fast degradation after emission." I don't agree with this statement as aromatics tend to have similar chemical reactivity as alkenes.

Response: We agree that the reactivities for some alkenes and aromatics are similar, but it may not be suitable for our observation. During this observation based on PTR, the most abundant alkenes are 1-hexene and isoprene, with the k_{OH} of 37 and 100×10^{-12} cm^3 $molecule^{-1}s^{-1}$, respectively. As for aromatics, the most abundant species are benzene, toluene and xylene, with the k_{OH} of 1.22, 5.63 and 17 cm^3 $molecule^{-1}s^{-1}$, respectively. Therefore, the reactivities of the observed alkenes are much higher than that of aromatics during this period in the study area. Hence, the relatively smaller change of OFP form alkenes could be explained by their chemical reactivities. To avoid misunderstanding, we have revised descriptions into:

During the observation, the most abundant alkenes measured by PTR-TOF-MS are 1-hexene and isoprene, with the k_{OH} of 37 and 100 $\times10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}, respectively， which are much higher than that of the most abundant aromatics (1.22, 5.63, and 17 cm^3 $molecule^{-1}$ s^{-1} for benzene, toluene, and xylene, respectively). The fast degradation of these alkenes could attribute to the small relatively smaller change of OFP from alkenes.

Line 277-278: This could also be due to enhanced solar radiation and temperature from January to March.

Response: We totally agree. The corresponding description has been revised, please refer to Line 303-304:

which could be attributed to the higher AOC, enhanced solar radiation and temperature during Partial-lockdown period.

Line 281-282: "This result suggests that the VOCs in Partial-lockdown should produce less O3 than that in Pre-lockdown, and Partial-lockdown period". This is misleading. First, the former

“Partial-lockdown” should be Full-lockdown. Second, the MIR that you calculate here refers to the ability of VOC species composition to produce ozone, is it correct? Thus, I suggest to further explain the concept of MIR and change this sentence into “This result suggests that VOC species composition in Full-lockdown is more conducive to ozone formation………”. In addition, please specify each dot represent 1-hour average or 24-hour average in Figure note.

Response: Thanks for pointing this out. The former “Partial-lockdown” has been revised to “Full-lockdown”. Yes, the MIR calculated here refers to the ability of VOC species composition to produce ozone. To avoid misleading, we have explained the concept of MIR, and this sentence has been revised as suggested, please refer to Lin 304-311. In addition, we have specified that the dot are 1-hour averaged in the note of Figure 7.

To compare the average reactivity of VOCs during different periods, we calculated the mean MIR, derived by dividing the total OFP by total VOC concentration, in each period. A higher MIR means stronger capability of VOCs to produce ozone. As shown in Figure 7, the average MIR during Pre-lockdown, Full-lockdown, and Partial-lockdown period was 3.85, 3.53 and 3.68 (g O_3/g VOC), respectively. This result suggests that VOC species composition in Full-lockdown is more conductive to ozone formation than that in Pre-lockdown, and Partial-lockdown period. However, the formation of O_3 was sensitive to the ratio of NO_x/VOCs and meteorological conditions, which can be significantly different in each period.

Line 304: “Feb 14th ” should be “Feb 1st”.

Response: We have revised this sentence as suggested.

Line 325-327: I suggest to explain the reason why OVOC kept stable among the three cases, which is inconsistent with the remarkable difference in measured OVOC among the three periods as you shown in Figure 4.

Response: Thanks for the suggestion. The original description is inaccurate. After double check of the data, we found that during the three periods, the k_{OH} and concentration of OVOC exhibited similar ”U-shaped” trend, with the minimum during Full-lockdown period. To avoid misleading, this sentence has been revised:

As k_{OH} from OVOC, it shared same trend as OVOC concentration, which reached the minimum value (5.56 s^{-1}) during the Full-lockdown period.

Line 330-355: PTR-TOF-MS is unable to measure alkanes and most alkenes, which could influence the diagnosis of ozone sensitivity to precursors. Lower VOCs concentrations lead to more VOC-limited regime. I suggest to provide uncertainty analysis about it.

Response: Thanks for the comment. To investigate the influence of the deficiency of C2~C5 alkenes and alkenes, we used the hypothetical diurnal variation of ethene, propene, butene, ethane, propane and butane as mentioned above and conducted EKMA analysis. Generally, adding C2~C5 alkenes and alkanes in the model would lead to slight increase of the simulated O_3, and could not obviously change the shape of O_3 isopleth (Figure 5). Therefore, the influence of the deficiency of C2~C5 alkenes and alkanes on the O_3 formation sensitivity is negligible. It should be noted that, this sensitivity analysis is based on the “hypothetical” diurnal variation of C2~C5 alkenes and alkanes, which would bring in uncertainty. We hope a wider range of VOCs would be monitored simultaneously in future field campaign and avoid this dificiency. The relative description has been added in the revised manuscript, please refer to Page 22, Line 431-437:

In addition, the deficiency of C2~C5 has potential to cause uncertainty in O_3 formation potential. To quantify this impact, the EKMA analysis with the hypothetical diurnal variation of C2~C5 was also performed. Generally, adding C2~C5 alkenes and alkanes in the model would lead to slight increase of the simulated O_3, and could not obviously change the shape of O_3 isopleth (Figure S9). Therefore, the influence of the deficiency of C2~C5 alkenes and alkanes on the O_3 formation sensitivity is negligible. It should be noted that, this sensitivity analysis is based on the “hypothetical” diurnal variation of C2~C5 alkenes and alkanes, which would bring in uncertainty. We hope a wider range of VOCs would be monitored simultaneously in future field campaign and avoid this deficiency.

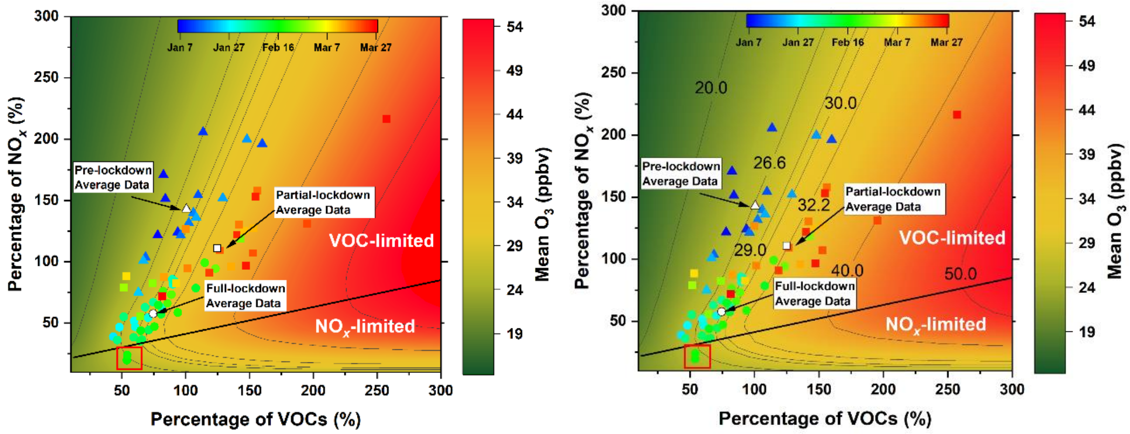

Figure 5. MeanO_3 isopleth with (left) and without (right) hypothetical diurnal variation of C2~C5 alkenes and alkanes. The colored circles, triangles, and rectangles represent the daily average

Figure 2: The legend of different parameters at the top of the Figure should be placed in corresponding sub-panels. Besides, the legend of ozone and TVOC is not given at present.

Response: The legend of each parameter was placed in corresponding sub-panels. In addition, the legend of O_3 and TVOC has been revised to be more conspicuous.

Section 2.2: How were photolysis frequencies been considered in the model? Were they constrained by photolysis measurements or calculated by a radiative transfer model (e.g., TUV)? If they were calculated, what about the uncertainty compared to the real condition? And what would be the influence on the afterwards data analysis?

Response: The photolysis frequencies (J values) were calculated as a function of solar zenith angle, altitude using lookup tables, calculated using the Tropospheric Ultraviolet and Visible (TUV) model, and relative description has been added in the revised manuscript. Since no observational data of J value is available, it is unable to calculate the uncertainty. Here, we only analyze the sensitivity of the simulated O_3 to J values by increasing or decreasing the photolysis rates by 10% and 20%. Results show that the simulated O_3 could decrease or increase by 25.14% or 21.73%, respectively, when photolysis rates were decreased or increased by 20% (Figure 6). In addition, the J values, which directly or indirectly influence the recycling of RO_x, could lead to uncertainty to the calculation of AOC and k_{OH}. The relative changes in AOC and k_{OH} by 1% changes in J values was 1.07%/% and 0.14%/%, respectively. Therefore, synchronously measurement of J values is recommended for future field campaign. Relative description has been added in the revised manuscript. Please refer to Page 23, Line 435-444:

Secondly, the photolysis frequencies (J values) were calculated as a function of solar zenith angle, altitude using lookup tables, calculated using the Tropospheric Ultraviolet and Visible (TUV) model, which could lead to uncertainty in the simulation of O_3. Hence, we analysis the influence of J values by increasing or decreasing the photolysis rates by 10% and 20%. Results showed that the simulated O_3 could decrease or increase by 25.14% or 21.73%, respectively, when photolysis rates were decreased or increased by 20% (Figure S10). In addition, the J values, which directly or indirectly influence the recycling of RO_x, could lead to uncertainty in the calculation of AOC and k_{OH}. Based on above sensitivity analysis, we found the relative changes in AOC and k_{OH} by 1% changes in J values was 1.07% and 0.14%, respectively. Therefore, the J values is recommended to be measured during future observations.

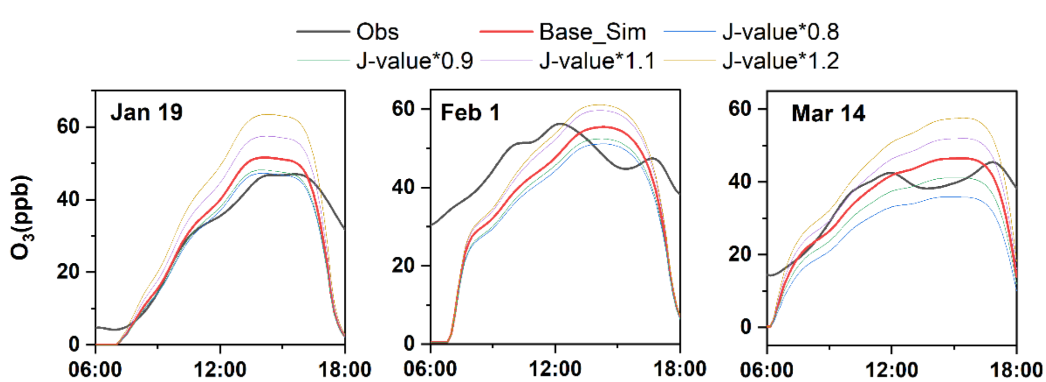

Figure 6. Uncertainty analysis of J-value

Line 375-376: “underestimation of ozone sensitivity to alkanes and alkenes” should be “underestimation of ozone production from alkanes and alkenes”.

Response: We have revised this sentence as suggested.