

Response to Interactive comment on “Ozone production in four major cities of China: sensitivity to ozone precursors and heterogeneous processes” by L. K. Xue et al.

Anonymous Referee #3

General comment and recommendation:

This study investigated ozone chemistry at four cities in China. Measurements from 4 field observation campaigns were analyzed using an OBM model. The value of a dataset consisting of in-situ measurements from 4 field campaigns is significant. However, it seems to me that this work is merely a collection of four independent case studies. The authors did not make an in-depth cross-case analysis and, thereby, I cannot see how a case relevant to the others. Such a “report” could be useful to formulation of air quality control strategy in China; however, I did not see scientific merits to support it published as an ACP paper. Furthermore, there are indeed some major flaws in the data analysis and interpretation as listed in the followings. Thus I recommend reject this submission.

Response: we would like to thank the reviewer for the critical comments, which have helped us to improve this study considerably. We have conducted further analysis to address all the comments made, by which the manuscript will be significantly improved. The major concerns of the reviewer are on (1) the ‘flaw’ in the analysis of transport vs. in-situ O₃ production and (2) the lack of ‘cross-region analysis’. We first address these two main concerns below and then make itemized responses to the specific comments.

(1) Brief response to the ‘flaw’ in the “ $R_{\text{chem}}-R_{\text{trans}}-R_{\text{meas}}$ ” analysis (see [Response to Comment 1](#) for more details)

The concern that the calculation of R_{meas} (for O₃) and R_{chem} (for total oxidant, or O_x) was inconsistent is relevant. **We will revise this analysis by correcting the R_{chem} calculation.** We have re-run our models for all of the cases to **directly calculate the net production rates (R_{chem}) of O₃** instead of O_x. This makes the R_{chem} consistent with the R_{meas} (both for O₃ now), and thus makes the estimated R_{trans} to be a sound measure of the transport effect. The major original conclusions still hold with the revised analysis, as O₃ generally dominated the O_x during our photochemical episodes. We will also update the whole manuscript with the new model calculations.

(2) Brief response to the ‘cross-region’ analysis (see [Response to Comment 4](#) for more details)

First we would like to state the rationale of the present study. Actually all the field studies were conducted within the framework of one project, which was aimed at understanding the regional processes and impacts of typical megacities in China. We targeted these four cities in different regions and with different climates and emissions, and wanted to compare their

pollution and processes. We utilized the same set of measurement techniques and models in order to reduce the uncertainties of the methodology. We indeed found differences among the four cities both in the O₃ precursor distributions from observations (i.e., dominance of alkenes in VOCs in Lanzhou, aromatics in Guangzhou, and aromatics & alkenes in Shanghai and Beijing) and in the O₃-precursor relationships from modeling analysis (i.e., aromatics-/alkenes-controlled in Shanghai, aromatics-controlled in Guangzhou, and mostly NO_x-controlled in Lanzhou).

Furthermore, after considering the review comments (they are indeed very helpful), we conducted modeling analysis for more cases to assess the impacts of heterogeneous processes. We do find some more interesting results. We found different impacts of the heterogeneous processes among the four cities, corresponding to the different distributions in aerosol surface and nitrogen oxides. For example, the N₂O₅ hydrolysis seems more significant in Shanghai due to its high levels of both aerosol and NO_x; the HO₂ loss should be more relevant for Beijing because of its higher aerosol surface loadings; the heterogeneous HONO formation is more important for Guangzhou and Shanghai mainly owing to their high NO_x levels; and Lanzhou seems to be less sensitive to all these processes due to relatively low concentrations of aerosol and NO_x. These findings do indicate some unique chemical processes occurring in different regions. A detailed description and the figures are provided in the Response to Specific Comment 4.

Given all of the above, we believe that our results should be helpful not only for air pollution control strategy but also for understanding the photochemical processes (especially heterogeneous processes) in China. We believe that our manuscript should be of interest for the readership of ACP, especially those of this “East Asian Megacity Special Issue”.

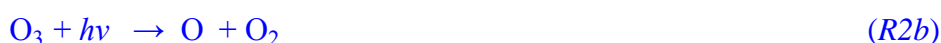
Specific comments:

1. *The contribution of urban plumes to ozone pollution in downwind areas was evaluated using a simple equation, $R_{trans} = R_{meas} - R_{chem}$ (Sec 3.2). Note that the term of in-situ photochemical ozone production (EQ1) is actually defined as the oxidation of NO by XO₂, which means production of NO₂ and in turn all the products relevant to the “O” from NO₂ photolysis (usually defined as total oxidant). This is why the loss term of ozone (EQ2) including not only ozone but also other major oxidants. In the calculation of R_{trans} , R_{meas} is the changes in ozone, whereas R_{chem} is theoretically defined on “total oxidant”. Thus the calculated R_{trans} cannot be a measure of transport effect because it includes many other factors relevant to chemical equilibrium among oxidants, titration reaction of O₃ and NO for instance. In this context, all the conclusions drawn from R_{trans} analysis could be false, or true but based on wrong inferences.*

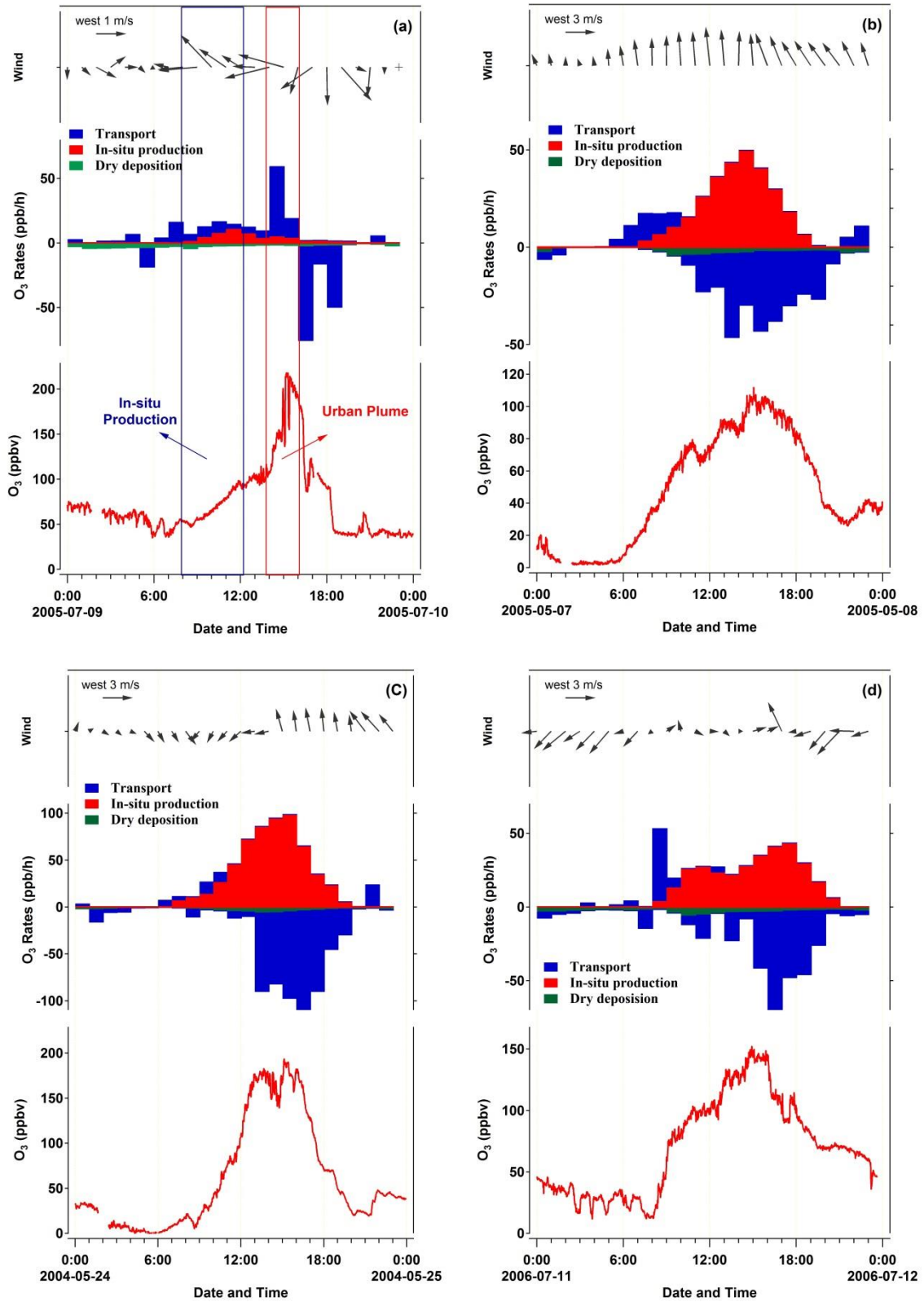
Response: the concern of the inconsistency between R_{meas} (for O₃) and R_{chem} (for O_x) is relevant and important to address. We had considered this issue before, but did not take it into

account given the fact that the O_x is predominately in the form of O_3 during our O_3 episodes. However, we had not made an in-depth analysis of the assumption we adopted that O_x can be approximated as O_3 . After considering the reviewer's comment, we will revise this analysis by correcting the calculation of R_{chem} as follows.

We have re-run our models for all of the episodes to directly calculate the net production rate of O_3 . The O_3 production is eventually achieved by the combination of O with O_2 (R1), and the O_3 destruction is mainly contributed by O_3 photolysis (R2), reactions with NO (R3), NO_2 (R4), OH (R5), HO_2 (R6), atoms of O (R7) and Cl (R8), and unsaturated VOCs (R9). The O_3 production, destruction and net rates can be then calculated from these reactions.



With the newly calculated " R_{chem} ", we re-estimated the " R_{trans} " using the equation " $R_{trans} = R_{meas} - R_{chem} - R_{dep}$ " (note that the dry deposition rate of O_3 , R_{dep} , is now calculated separately within our model). As R_{meas} , R_{chem} and R_{dep} are all the rates for O_3 , the R_{trans} should be a measure of the transport effect for O_3 . The revised Figure 5 is also provided below. It shows that our original main conclusions still hold with the revised calculation of R_{chem} in that regional transport contributes to the O_3 pollution at the Beijing site while in-situ production dominates at the other three sites. All of the other discussion related to the model calculations will be also updated in the revised manuscript.



Revised Figure 5. Accumulation of O_3 and contributions from *in-situ* chemistry and transport during O_3 episodes in (a) Beijing (July 9, 2005), (b) Shanghai (May 7, 2005), (c) Guangzhou (May 24, 2004), and (d) Lanzhou (July 11, 2006). The blue bars are added to the red bars.

2. Moreover, it was mentioned that “the atmospheric mixing was also included here”. However, it’s unclear throughout the paper how the atmospheric dynamics was considered in this work. Dynamics of mixing layer could be one of the major mechanisms responsible for the drastic changes in R_{trans} , as shown in Fig 5. (There was no discussion explaining those spikes or sudden changes in R_{trans} in the maintext.)

Response: the original sentence may be misleading. The more correct statement should be “the effect of atmospheric mixing was also included in the ‘ R_{chem} ’ term”. We didn’t consider the atmospheric mixing process per se in our box model. By subtracting “ R_{chem} ” (chemistry effect) from “ R_{meas} ” (net effect), we use “ R_{trans} ” to represent the effects of regional transport as well as atmospheric mixing.

Indeed we recognize, the dynamics of the mixing layer should be a major mechanism responsible for the R_{trans} changes. For instance, R_{trans} does represent an important contributor to the O_3 increase during the early morning period at all four sites, especially for the Lanzhou case (see the above Fig. 5), and can be attributed to mixing with the air aloft when the nocturnal boundary layer breaks down.

The sudden changes in R_{trans} were mainly due to the changes in winds. During the Beijing case (see Fig 5a), for example, the southeasterly winds brought the urban plume to the study site, resulting in an O_3 peak at 14:00–15:00; but after that the wind direction shifted to northerly and blew back the plume, leading to a sharp decrease in O_3 levels. Similar wind effects were also found from the Guangzhou and Lanzhou cases (see Fig 5c and 5d).

We will adopt the reviewer’s comment and add a discussion in the revised manuscript.

3. The sensitivity of ozone to precursors in three of the four cases was discussed in Sec 3.3. Why did you drop out the case of Beijing?

Response: The end of Section 3.2 indicated why we only discussed the O_3 -precursor relationships in Shanghai, Guangzhou and Lanzhou, but it may be not clear enough. The reason we excluded the case of Beijing is that the O_3 increase at the Beijing site was mainly contributed by the regional transport of urban plumes. The OBM analysis of the O_3 -precursor relationship is only relevant to the in-situ production, which was only a small fraction for the Beijing case. We will elaborate this in the revised manuscript.

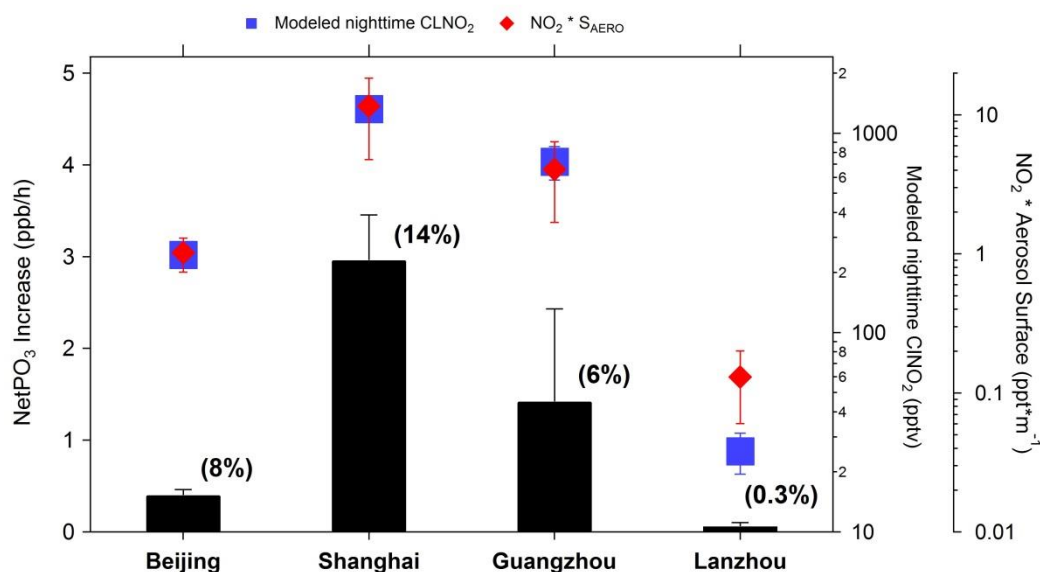
4. At the end of Sec 3.3, the authors claim that this study is a good effort as a cross-region comparative study. However, again, I did not find any real “cross-region” analysis in addition to lumping four cases in one article.

Response: we think the word “cross-region” may be somewhat misleading here. The original aim of the present study was to compare the photochemical pollution and processes in four different regions by use of the data collected by the same measurement techniques. And we did find some differences not only in the VOC distributions from the observations (i.e.,

dominance of alkenes in Lanzhou, aromatics in Guangzhou, and both aromatics and alkenes in Shanghai and Beijing) but also in the O₃-precursor relationships from the modeling analysis (i.e., aromatics-/alkenes-limited in Shanghai, aromatics-limited in Guangzhou, and almost NO_x- limited in Lanzhou). These results deepen the understandings of the O₃ production and VOC reactivity in large cities of China.

Moreover, we do find some unique heterogeneous processes which are relevant for some regions but may be not for the others, depending on the abundances of aerosol surface and/or nitrogen oxides. Specifically, the N₂O₅ hydrolysis was more important for the Shanghai site with high levels of both aerosol and NO_x; the HO₂ loss was more relevant for the Beijing site because of its highest aerosol surface concentrations; the heterogeneous HONO formation is important for the Guangzhou and Shanghai sites mainly due to the high levels of NO_x; and all these processes seemed to be less sensitive for Lanzhou owing to the relatively low aerosol loadings and NO_x. These findings indicate some unique processes in different regions of China.

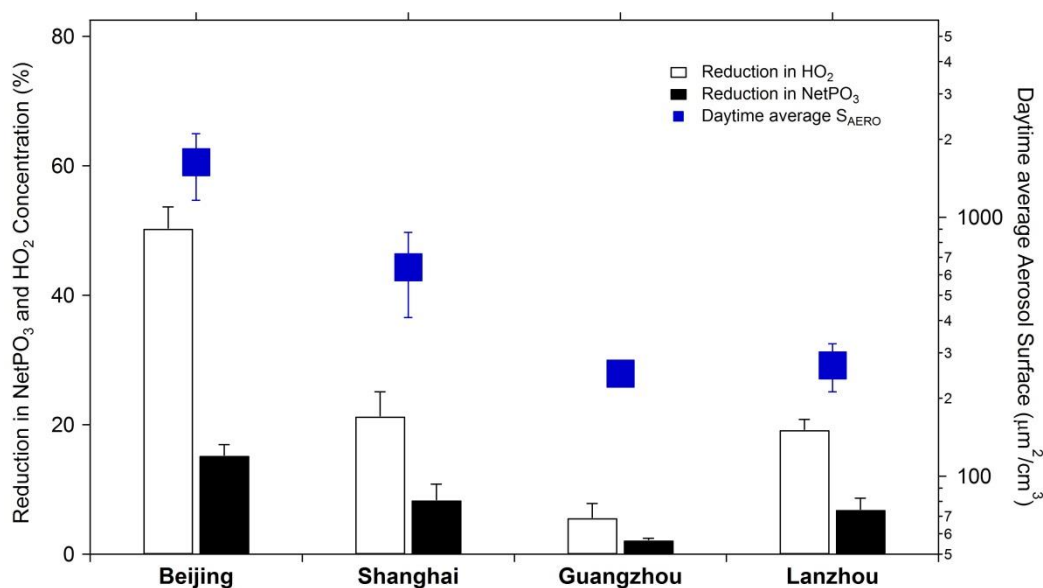
The new results on the heterogeneous processes as well as the related figures (with a brief discussion) are attached below. We will include them in the revised manuscript.



Revised Figure 8. Average increase in the daytime-average O₃ production rates by including the CLNO₂ formation ($\phi_{\text{CLNO}_2}=0.6$; compared to $\phi_{\text{CLNO}_2}=0$) during the episodes at four cities. Also shown are the model-simulated nighttime concentrations of CLNO₂ as well as the product of NO₂ with aerosol surface. The error bars are standard deviations. The number in parentheses gives the increase in percentage.

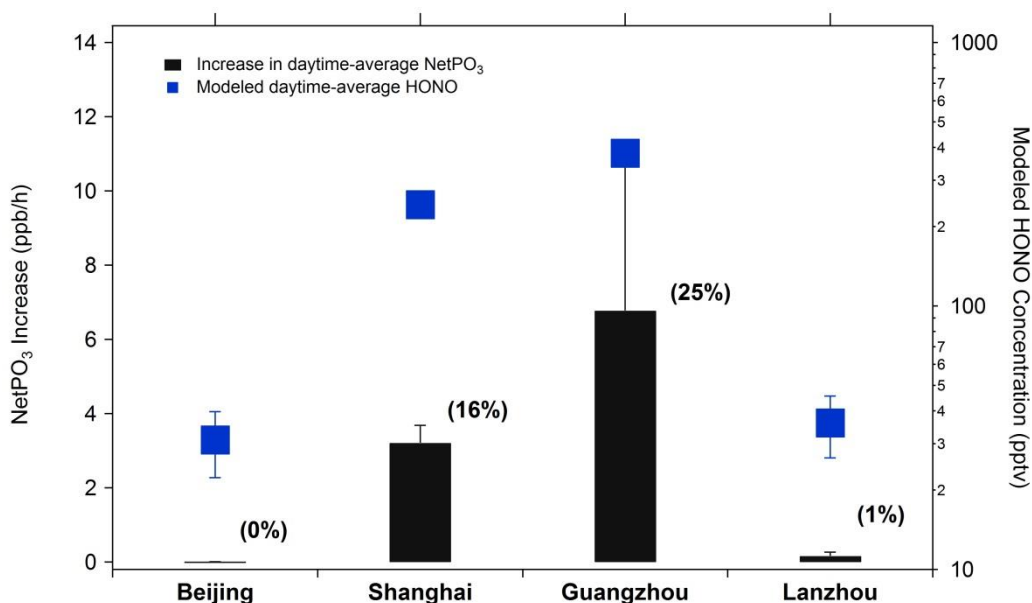
The revised Fig. 8 shows the impacts of the CINO₂ formation through N₂O₅

hydrolysis on the O_3 production as well as its dependence on the aerosol surface and nitrogen oxides. We can see that including $ClNO_2$ formation would enhance the daytime-average O_3 production rates during the three episodes in Shanghai by ~ 3 ppb/h on average (or $14\% \pm 3.9\%$ in percentage). This impact highly depends on the abundances of both aerosol surface area (more interface) and nitrogen oxides (more reactants).



Revised Figure 9. Average reductions in the daytime-average HO_2 concentrations and O_3 production rates by adjusting γ_{HO_2} from 0.02 to 0.4 during the episodes at four cities. Also shown are the observed aerosol surface concentrations (note that the data in Guangzhou was inferred from the measurements at a nearby station in Hong Kong). The error bars are standard deviations.

The revised Fig. 9 shows the effects of heterogeneous HO_2 loss on the HO_2 concentrations and O_3 production as well as its dependence on the aerosol surface. We can see that adopting a higher uptake coefficient ($\gamma_{HO_2} = 0.4$) would reduce significantly the HO_2 concentrations at the Beijing site (almost 50%) due to its very high loading of aerosol surface ($\sim 1600 \mu m^2/cm^3$). Such HO_2 reduction would in turn result in an average reduction of 15% ($\pm 1.7\%$) in the daytime-average O_3 production rates (A relatively smaller reduction in O_3 production at our rural site may be a result of the O_3 production being more sensitive to NO_x).



Revised Figure 10. Average increase in the daytime-average O₃ production rates by including HONO formation from heterogeneous NO₂ reactions during the episodes at four cities. Also shown are the modeled daytime-average HONO concentrations. The error bars are standard deviations. The number in parentheses gives the increase in percentage.

The heterogeneous reactions of NO₂ affect O₃ production by consuming NO₂ (negative effect) and releasing OH via HONO photolysis (positive effect), and the net effect depends on their balance. The revised Fig. 10 shows the impacts of the NO₂ heterogeneous reactions on the O₃ production during the episodes at four cities. We can see that including these processes would enhance the daytime-average O₃ production rates by 6.8 ppb/h and 3.2 ppb/h on average (25%±10% and 16%±2%) in Shanghai and Guangzhou, respectively. This impact mainly depends on the abundance of nitrogen oxides (aerosol surface seems not a key factor here, which may be due to the fact that the heterogeneous HONO formation on the ground surface generally dominates than those on aerosol surface).

5. *Heterogeneous reactions were discussed in Sec 3.4. However, as the paper entitled as a study of four cities, only a 1-day case of Shanghai was discussed for N₂O₅ and HO₂ chemistry, and another 1-day case of Guangzhou for HONO reactions. I disagree that the two cases can be representatives of the complicated atmospheric chemistry in urban areas.*

Response: after consideration of this comment, we have conducted a more extensive analysis for all of the cases at all four cities (by which we found some new interesting results as described in our response to Comment 4 above). The data shown in the revised Figures 8-10 (see above) are averages (with standard deviations) of the results determined for all the

episodes in individual cities. In addition, we also conducted the same analysis with the campaign-average data which should reflect to some extent the **general conditions** of the four cities, and the results are consistent with those determined for the episodes. The Section 3.4 will be largely modified and improved in the revised manuscript.

6. The work of Sec 3.4 is to investigate the responses of ozone production to N₂O₅ hydrolysis, HO₂ uptake by aerosols, and HONO from surface reactions of NO₂, respectively. In a model study, adding a source or sink reaction will certainly result in a corresponding outcome and the scientific question is how significant the outcome change due to the inclusion of a new factor. In all the three case studies presented here, the ozone production changed by ~10% only as compared to the respective control runs. The authors claimed that the changes were significant. However, I think the conclusions cannot be drawn before the uncertainties associated to the simulations are carefully evaluated.

Response: as stated above, we have conducted more in-depth analysis to assess the potential impacts of the heterogeneous processes. In the revised manuscript, we will focus on the cases with relatively high ozone production changes, *i.e.*, **14% – 25%** (see the above Figures 8–10). Compared with the base model runs, we only made the one change to include the target heterogeneous process, with the assumption that the other processes/uncertainties would remain the same in both scenarios. Given the many processes that can affect the ozone production, we think the sensitivity to ozone production changes by 14% – 25% resulting from a single process should be **considerable**.