

## Response to Reviewer 2:

*General Comment: The impact of the O&NG exploration on the O<sub>3</sub> formation in both summer and winter is one of the key issues in the studies of tropospheric chemistry. Negative impact of the O&NG exploration in North America had already been presented in a series of field studies in both United States and Canada including the warnings of serious wintertime ozone non-attainment for the Basin landscape. The study of O&NG exploration on the atmospheric chemistry is missing in China and has been nicely filled up by the current paper based on winter and summer field studies in Yellow River Delta (YelRD) which is a place famous for open oil fields in China. The dataset obtained in this study are very valuable and the data analysis is systematic and scientifically sound. The paper has been clearly written. Overall, I suggest to publish the paper after the authors addressed the following comments.*

**Response:** we appreciate the reviewer for the positive comments and helpful suggestions. We have carefully considered and addressed all of these comments, and revised accordingly the original manuscript. Below we provide the original referee's comments *in black italics*, with our responses and changes in the manuscript in blue and red, respectively.

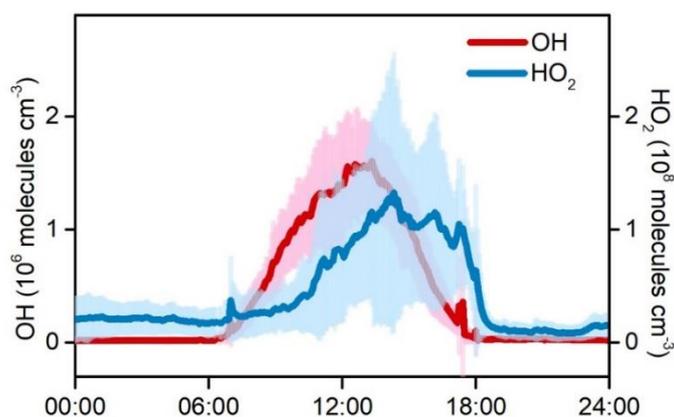
### **Major Comment**

*1. It will be very valuable for the current paper to analyze the radical budget and the ozone production rates also for the winter campaign. And compare with the corresponding US studies to show from a chemical perspective why the ozone pollution is not appeared in the YelRD region.*

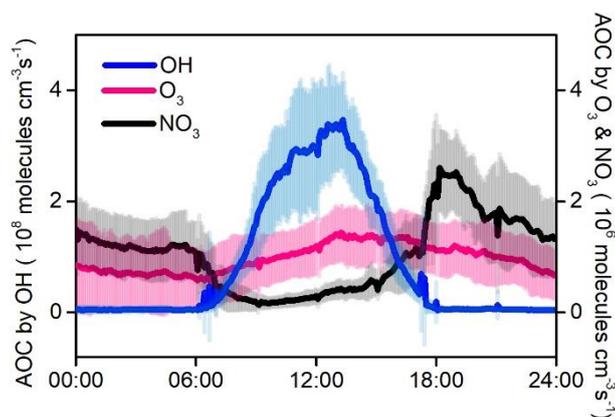
**Response:** thanks for the helpful suggestion. We have performed the same modelling analyses for eight winter-spring cases. Since few ozone episodes were encountered in winter and early spring in this study, the cases were selected mainly due to the availability of multiple NMHCs and carbonyl sampling data. The daily maximum hourly O<sub>3</sub> concentrations ranged from 40 to 98 ppbv during these cases. Overall, the model-simulated HO<sub>x</sub> levels, AOC, RO<sub>x</sub> production and recycling rate, and O<sub>3</sub> formation rate on the winter-spring cases (see Figures below) were much lower than those during the summertime O<sub>3</sub> episodes in the YelRD region as well as during the wintertime O<sub>3</sub> episodes in U.S. oilfield basins. We also compared the similarity and differences in the radical budget between winter-spring and summer. The following discussions have been added in the revised manuscript, with Figures R1-R6 being provided in the revised supplement.

“We also examined the atmospheric oxidation capacity, RO<sub>x</sub> radical budget, and O<sub>3</sub> formation for eight winter-spring cases, and the modelling results are documented in Figures S2-S7. Note that few O<sub>3</sub> episodes were encountered during the winter-spring campaign, and the cases were

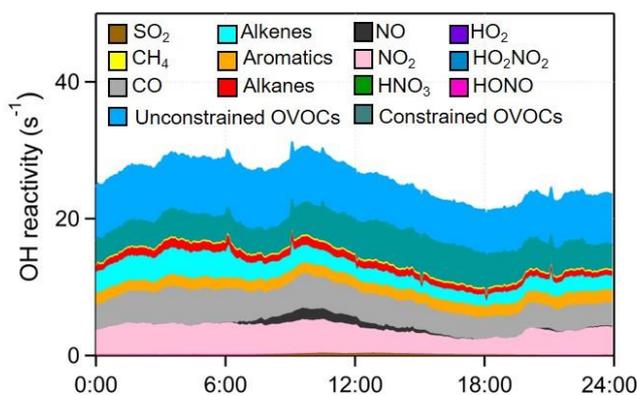
selected mainly because of the availability of multiple NMHCs and carbonyls sampling data. The daily maximum hourly  $O_3$  concentrations during these cases were in the range of 40-98 ppbv. Several aspects are noteworthy from the modelling results for winter-spring. First, the model-simulated  $HO_x$  levels, AOC,  $RO_x$  production and propagation rates, and  $O_3$  formation rate were much lower than those determined for the summertime episodes. This is as expected due to the weaker solar radiation and less active photochemistry in winter-spring than in summer. Second, OH showed a ‘normal’ noontime concentration peak in winter-spring, which is different from the morning peak (~10:00 LT) found in summer (see Figs. 8 and S2). This was ascribed to the higher levels of  $NO_x$  at the study site in winter-spring (Fig. 3), which were high enough to maintain the radical recycling from  $HO_2$  to OH. Third, the partitioning of the primary  $RO_x$  sources were generally similar between both seasons, despite the relatively lower contributions from the  $O_3$ -involved sources (i.e.,  $O_3$  photolysis and  $O_3$ +VOCs reactions). Photolysis of OVOCs other than formaldehyde was the dominant primary  $RO_x$  source, followed by HONO and formaldehyde photolysis. Fourth, the radical termination processes were different between winter-spring and summer. The dominant radical sinks were the cross reactions between  $NO_x$  and  $RO_x$  in winter-spring, as a result of the relatively abundant ambient  $NO_x$ .”



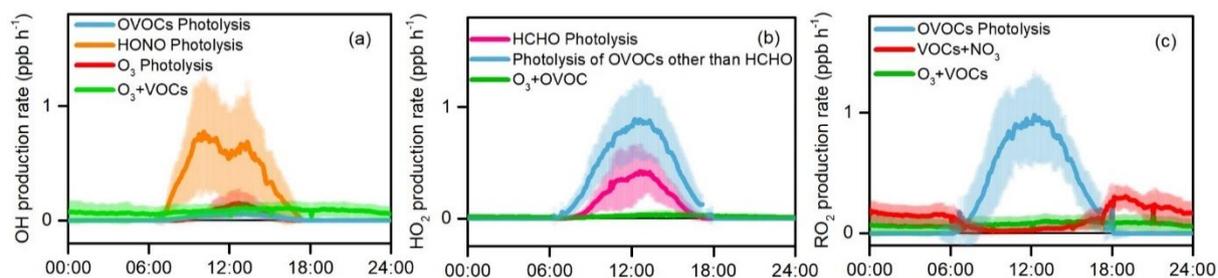
**Figure R1.** Model-simulated average diurnal variations of OH and  $HO_2$  during the eight selected cases in February-March 2017. The shaded areas indicate the standard deviations of the mean.



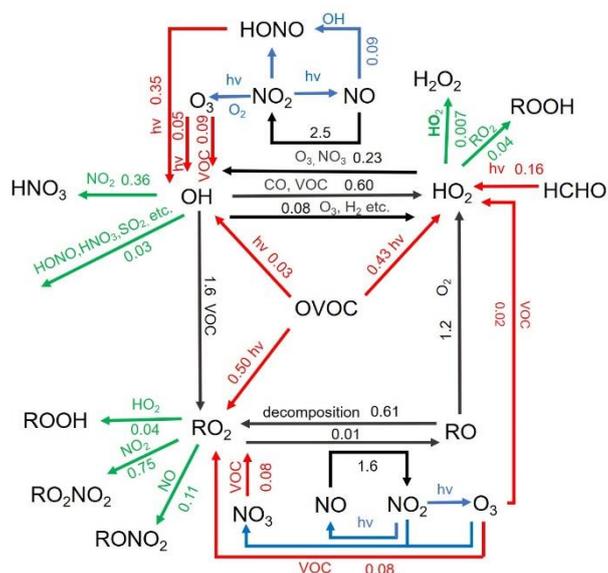
**Figure R2.** Model-calculated average oxidation capacity of OH, O<sub>3</sub> and NO<sub>3</sub> during the eight selected cases in February-March 2017. The error bars indicate the standard deviations of the mean.



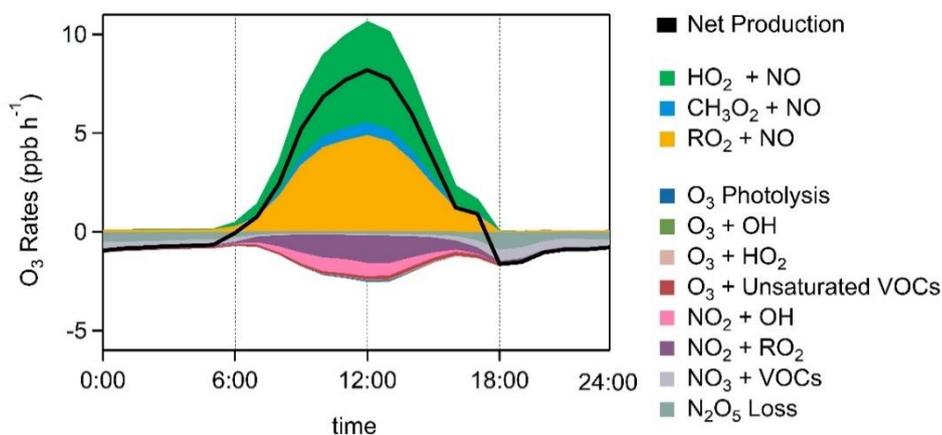
**Figure R3.** Model-calculated average OH reactivity ( $K_{OH}$ ) and its breakdown to the major reactants during the eight selected cases in February-March 2017.



**Figure R4.** Model-simulated average primary production rates of (a) OH, (b) HO<sub>2</sub>, and (c) RO<sub>2</sub> during the eight selected cases in February-March 2017. The error bars indicate the standard deviations of the mean.



**Figure R5.** Daytime average (6:00-18:00 LT) RO<sub>x</sub> budget during the eight selected cases in February-March 2017. The unit is ppb h<sup>-1</sup>. The red, green and black lines indicate the production, destruction and recycling pathways of radicals, respectively.



**Figure R6.** Simulated average O<sub>3</sub> budget during the eight selected cases in February-March 2017.

### **Specific Comment**

1. Page 6, lines 1- 6, as described by the authors, the VOC samples were analyzed in the US lab which is far away. How did the authors make sure that the reactive compounds are not decayed away during the time span between sampling and the lab analysis?

**Response:** the canisters were shipped to the US lab immediately after the field campaign, and were analyzed within two weeks. Indeed, some reactive compounds may be inevitably decayed more or less during the time span between sampling and lab analysis. We have stated this potential uncertainty of our VOC analysis in the revised manuscript, as follows.

“Note that O<sub>3</sub> scrubbers were not used ahead of the canisters during the sampling, and the sampled canisters were shipped to the UCI for analysis immediately after the individual field campaign. Some reactive VOC compounds (such as alkenes) may be decayed more or less during the time span from sampling to lab analysis. Thus, one should keep in mind that the VOC observations in this study may be subject to some uncertainty and the reactive compounds may be underestimated to some extent.”

2. The authors used “Atmospheric Oxidative Capacity” (page 6, line 17; page 11, line 17), “Atmospheric Oxidizing Capacity” (page 6, line 28; page 12, line 13), to denote AOC. I suggest the authors to use “Atmospheric Oxidation Capacity” for that. At least, it should be unified throughout the paper.

**Response:** “Atmospheric Oxidation Capacity” has been used uniformly to denote “AOC” throughout the revised manuscript.

3. Page 7, lines 9-11, I don't think the authors can refer the calculations of the ozone production rates simply to previous papers. The detailed equation needs to be given here and the uncertainty of the calculations is worth to be analyzed.

**Response:** the ozone production rate ( $P(O_3)$ ) was calculated as the sum of reaction rates for  $HO_2+NO$  and  $RO_2+NO$  reactions; the ozone loss rate ( $L(O_3)$ ) was calculated as the sum of reaction rates for  $O_3$  photolysis,  $O_3+OH$ ,  $O_3+HO_2$ ,  $O_3+VOCs$ ,  $NO_2+OH$ ,  $NO_2+RO$ ,  $NO_2+RO_2$  (minus the decomposition rate of organic nitrates),  $NO_3+VOCs$ , and loss of  $N_2O_5$ . The net  $O_3$  production rate can be calculated as the difference between  $P(O_3)$  and  $L(O_3)$ . Such calculated net ozone production rate actually denote the chemical production rate of  $O_x$  ( $O_x=O_3+NO_2$ ), and has been widely adopted in the previous studies. The detailed equations have been provided in the revised manuscript. The revised context is as follows.

“The  $O_3$  chemical budget was also quantified by the model.  $O_3$  production rate ( $P(O_3)$ ) was calculated as the sum of reaction rates for  $HO_2+NO$  and  $RO_2+NO$  reactions (E1), and  $O_3$  loss rate ( $L(O_3)$ ) was computed as the sum of reaction rates for  $O_3$  photolysis,  $O_3+OH$ ,  $O_3+HO_2$ ,  $O_3+VOCs$ ,  $NO_2+OH$ ,  $NO_2+RO_2$  (minus the decomposition rate of organic nitrates),  $NO_3+VOCs$ , and loss of  $N_2O_5$  (E2). The net  $O_3$  production rate can be calculated as the difference between  $P(O_3)$  and  $L(O_3)$  (E3). Where,  $k_i$  is the corresponding reaction constant.”

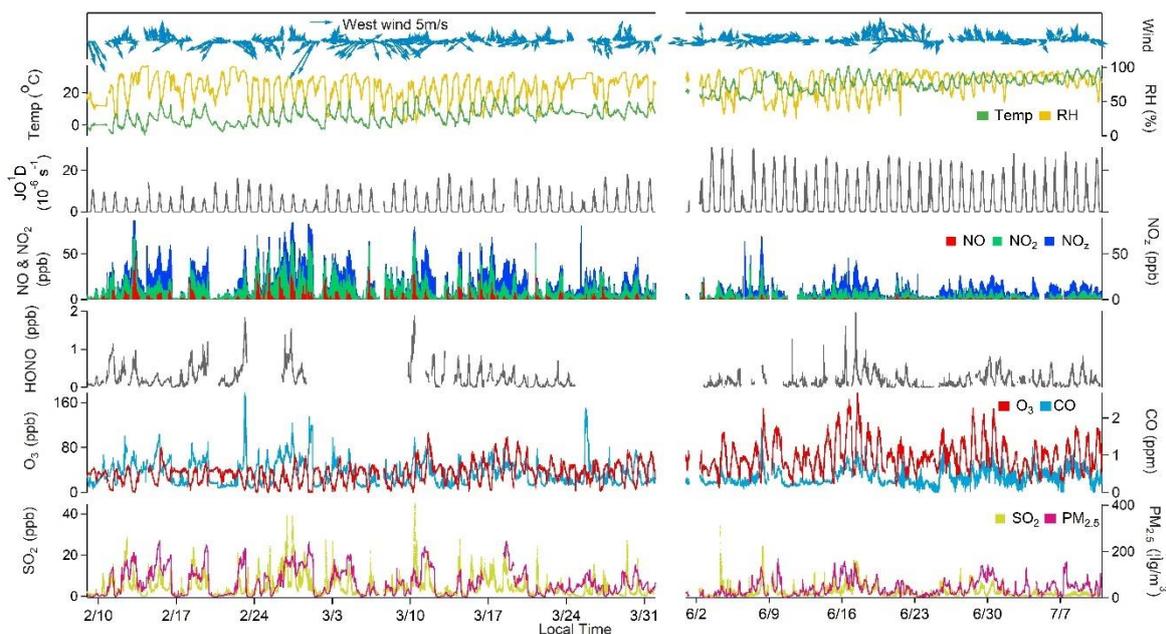
$$P(O_3) = k_1[HO_2][NO] + \sum(k_2[RO_2][NO]) \quad (E1)$$

$$L(O_3) = k_3[O^1D][H_2O] + k_4[O_3][OH] + k_5[O_3][HO_2] + \sum(k_{6i}[O_3][VOC_i]) + k_7[OH][NO_2] + \sum(k_{8i}[NO_2][RO_{2i}]) + 2\sum(k_{9i}[NO_3][VOC_i]) + 3k_{10}[N_2O_5] \quad (E2)$$

$$\text{net } P(O_3) = P(O_3) - L(O_3) \quad (E3)$$

4. Figure 2, Y title, ‘jOID’ the number 1 shall be superscript.

**Response:** Figure 2 has been revised as suggested, see below.



**Revised Figure 2.** Time series of major trace gases, PM<sub>2.5</sub>, and meteorological parameters measured at the study site during February-March and June-July 2017.

5. Figure 4, from the plot of the subgroups of the NMHCs, it is not clear to the readers how the high concentrations up to hundreds and thousands of ppbv of NMHCs is make up?

**Response:** we are sorry that the unit used in Figure 4 is incorrect. The unit should be ppm, other than ppb. The box plot provides the 5<sup>th</sup>, 25<sup>th</sup>, 50<sup>th</sup>, 75<sup>th</sup> and 95<sup>th</sup> of the measurement data. We have corrected this mistake in the revised manuscript.

6. Page 11, line 29 -30, why not compared your results to measurements of HO<sub>x</sub> radicals in NCP such as Tan et al., ACP, 2017. And Tan et al., ACP, 2018 needs updated (it is already published in ACP).

**Response:** thanks for the suggestion. We have compared our model prediction with the measured results of Tan et al. (2017), both of which are generally comparable. The following discussion has been added in the revised manuscript. The reference of Tan et al. (2018) has been updated.

“Comparable noontime maxima HO<sub>x</sub> concentrations were observed at a rural site in the NCP region (Wangdu; Tan et al., 2017) and in some polluted urban areas, such as Tokyo and Houston (Kanaya et al., 2007; Mao et al., 2010).”

Tan, Z., Fuchs, H., Lu, K., Hofzumahaus, A., Bohn, B., Broch, S., Dong, H., Gomm, S., Häsel, R., et al., 2017. ACP, 17, 11111–11127.

R., He, L., Holland, F., Li, X., Liu, Y., Lu, S., Rohrer, F., Shao, M., Wang, B., Wang, M., Wu, Y., Zeng, L., Zhang, Y., Wahner, A., and Zhang, Y.: Radical chemistry at a rural site (Wangdu) in the North China Plain: observation and model calculations of OH, HO<sub>2</sub> and RO<sub>2</sub> radicals, *Atmos. Chem. Phys.*, 17, 663–690, <http://doi.org/10.5194/acp-17-663-2017>, 2017.

Tan, Z., Lu, K., Hofzumahaus, A., Fuchs, H., Bohn, B., Holland, F., Liu, Y., Rohrer, F., Shao, M., Sun, K. and Wu, Y.: Experimental budgets of OH, HO<sub>2</sub> and RO<sub>2</sub> radicals and implications for ozone formation in the Pearl River Delta in China 2014, *Atmos. Chem. Phys.*, 2019, 7129–7150, <https://doi.org/10.5194/acp-19-7129-2019>, 2019.

7. Page 12, line 21 – 29, there were a number of direct total OH reactivity measurements published for field studies in NCP and PRD by the PKU and FZJ groups. I suggest the authors shall compare those in addition to the comparison to US cities. To my knowledge, the  $k_{OH}$  in this study is within the range of the available measurement in China.

**Response:** thanks for the suggestion. These direct total OH reactivity observation studies have been compared against our model calculations in the revised version. The following discussions and references have been added.

“ $k_{OH}$  in this study ( $23.3 \pm 5.6 \text{ s}^{-1}$ ) is significantly higher than those determined from some rural sites such as Hok Tsui ( $9.2 \pm 3.7 \text{ s}^{-1}$ ) (Li et al., 2018), Nashville ( $11.3 \pm 4.8 \text{ s}^{-1}$ ) (Martinez et al., 2003), and Whiteface Mountain ( $5.6 \text{ s}^{-1}$ ) (Ren et al., 2006a), and is comparable to those measured in some polluted areas like Beijing ( $10\text{-}30 \text{ s}^{-1}$ ) (Lu et al., 2013; Williams et al., 2016; Yang et al., 2017) and Guangzhou ( $20\text{-}50 \text{ s}^{-1}$ ) (Lou et al., 2010).”

Williams, J., Kessel, S. U., Nolscher, A. C., Yang, Y. D., Lee, Y., Yanez-Serrano, A. M., Wolff, S., Kesselmeier, J., Klupfel, T., Lelieveld, J., and Shao, M.: Opposite OH reactivity and ozone cycles in the Amazon rainforest and megacity Beijing: Subversion of biospheric oxidant control by anthropogenic emissions, *Atmos. Environ.*, 125, 112–118, 2016.

Lou, S., Holland, F., Rohrer, F., Lu, K., Bohn, B., Brauers, T., Chang, C. C., Fuchs, H., Häsel, R., Kita, K., Kondo, Y., Li, X., Shao, M., Zeng, L., Wahner, A., Zhang, Y., Wang, W., and Hofzumahaus, A.: Atmospheric OH reactivities in the Pearl River Delta – China in summer 2006: measurement and model results, *Atmos. Chem. Phys.*, 10(22), 11243–11260, [10.5194/acp-10-11243-2010](http://doi.org/10.5194/acp-10-11243-2010), 2010.

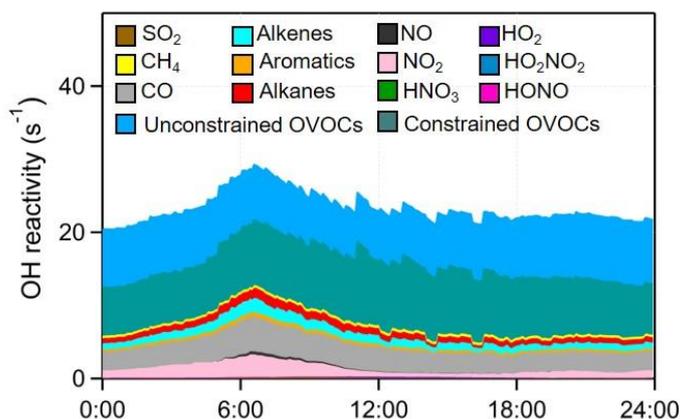
Lu, K. D., Hofzumahaus, A., Holland, F., Bohn, B., Brauers, T., Fuchs, H., Hu, M., Häsel, R., Kita, K., Kondo, Y., Li, X., Lou, S. R., Oebel, A., Shao, M., Zeng, L. M., Wahner, A., Zhu, T.,

Zhang, Y. H., and Rohrer, F.: Missing OH source in a suburban environment near Beijing: observed and modelled OH and HO<sub>2</sub> concentrations in summer 2006, *Atmos. Chem. Phys.*, 13(2), 1057–1080, <http://doi.org/10.5194/acp-13-1057-2013>, 2013.

Yang, Y., Shao, M., Keßel, S., Li, Y., Lu, K., Lu, S., Williams, J., Zhang, Y., Zeng, L., Nölscher, A. C., Wu, Y., Wang, X., and Zheng, J.: How the OH reactivity affects the ozone production efficiency: case studies in Beijing and Heshan, China, *Atmos. Chem. Phys.*, 17, 7127–7142, [10.5194/acp-17-7127-2017](http://doi.org/10.5194/acp-17-7127-2017), 2017.

8. Figure 10, a lot of OVOCs is calculated in the model. The summed reactivity is much higher than that of their precursors (alkanes, alkenes, and aromatics) which is normally difficult to achieve. The large accumulation of OVOCs in the model may be related with the lifetime of those OVOCs implemented in the model. Could the authors breakdown the speciation of the calculated OVOCs and compare with the measurements as mentioned in the part of methods. The comparison between model and measurements for OVOCs could help the authors to define the lifetime of the OVOCs in the model.

**Response:** thanks for the suggestion. Actually, the measured C<sub>1</sub>-C<sub>8</sub> carbonyl compounds have been used to constrain the box model. We calculated the  $k_{OH}$  contributed from the 14 measured carbonyls, and compared it with that of the other model-simulated OVOC compounds. Overall, the measured carbonyls contributed to the majority of the  $k_{OH}$  of total OVOCs, with an average fraction of 55%, while the other model-simulated OVOCs contributed to the remaining 45%. We also examined the lifetime of OVOCs implemented in the model. With a dry deposition velocity of 0.20-0.55 cm s<sup>-1</sup> and an assumed nocturnal mixing layer height of 300 m, the lifetime of OVOCs (only forced by dry deposition) at nighttime was estimated as 15-42 hours. In the revised manuscript, the original Figure 10 has been modified as follows, by separating the  $k_{OH}$  of total OVOCs into those contributed from the measured and simulated components.



**Revised Figure 10.** Model-calculated average OH reactivity ( $K_{OH}$ ) and its breakdown to the major reactants during the summertime O<sub>3</sub> pollution episodes.

9. Figure 11, the OH production rate from O<sub>3</sub> photolysis seems to be a little large according to your O<sub>3</sub> concentrations presented in Figure 3. I assume you calculated the photolysis rate of O<sub>3</sub> (O<sub>3</sub> + hv → O<sup>1</sup>D), but the OH production needs a further reaction with H<sub>2</sub>O (O<sup>1</sup>D + H<sub>2</sub>O → OH) which is competed by reaction with N<sub>2</sub> and O<sub>2</sub> (O<sup>1</sup>D+M→O), the yield of OH is often around 10% of the photolysis rate of O<sub>3</sub> depends on the H<sub>2</sub>O concentrations.

**Response:** the OH production rate from O<sub>3</sub> photolysis was calculated from the reaction “O<sup>1</sup>D + H<sub>2</sub>O = OH + OH” (as 2\*k\*[O<sup>1</sup>D]\*[H<sub>2</sub>O]). In the present study, the modelling analyses were only conducted for nine severe O<sub>3</sub> episode days, when the maximum hourly O<sub>3</sub> concentrations exceeding 100 ppb every day (the hourly O<sub>3</sub> peak values exceeded 110 ppbv on 8 episodes and exceeded 130 ppbv on 5 episodes). The data presented in Figure 3 were campaign average and largely lower than those on the episode days. The calculated OH production rate from O<sub>3</sub> photolysis in this study also fell in the range reported from the previous studies in some other polluted areas (e.g., Liu et al., 2012; Lu et al., 2013; Xue et al., 2016; Tan et al., 2017).

Liu, Z., Wang, Y., Gu, D., Zhao, C., Huey, L.G., Stickel, R., Liao, J., Shao, M., Zhu, T., Zeng, L. and Amoroso, A.: Summertime photochemistry during CAREBeijing-2007: RO<sub>x</sub> budgets and O<sub>3</sub> formation, *Atmos. Chem. Phys.*, 12, 7737–7752, <https://doi.org/10.5194/acp-12-7737-2012>, 2012.

Xue, L., Gu, R., Wang, T., Wang, X., Saunders, S., Blake, D., et al. (2016). Oxidative capacity and radical chemistry in the polluted atmosphere of Hong Kong and Pearl River Delta region: analysis of a severe photochemical smog episode, *Atmos. Chem. Phys.*, 16(15), <http://doi.org/10.5194/acp-16-9891-2016>, 2016.

Lu, K. D., Hofzumahaus, A., Holland, F., Bohn, B., Brauers, T., Fuchs, H., Hu, M., Häseler, R., Kita, K., Kondo, Y., Li, X., Lou, S. R., Oebel, A., Shao, M., Zeng, L. M., Wahner, A., Zhu, T., Zhang, Y. H., and Rohrer, F.: Missing OH source in a suburban environment near Beijing: observed and modelled OH and HO<sub>2</sub> concentrations in summer 2006, *Atmos. Chem. Phys.*, 13(2), 1057–1080, <http://doi.org/10.5194/acp-13-1057-2013>, 2013.

Tan, Z., Fuchs, H., Lu, K., Hofzumahaus, A., Bohn, B., Broch, S., Dong, H., Gomm, S., Häseler, R., He, L., Holland, F., Li, X., Liu, Y., Lu, S., Rohrer, F., Shao, M., Wang, B., Wang, M., Wu, Y., Zeng, L., Zhang, Y., Wahner, A., and Zhang, Y.: Radical chemistry at a rural site (Wangdu) in the North China Plain: observation and model calculations of OH, HO<sub>2</sub> and RO<sub>2</sub> radicals, *Atmos. Chem. Phys.*, 17, 663–690, <http://doi.org/10.5194/acp-17-663-2017>, 2017.

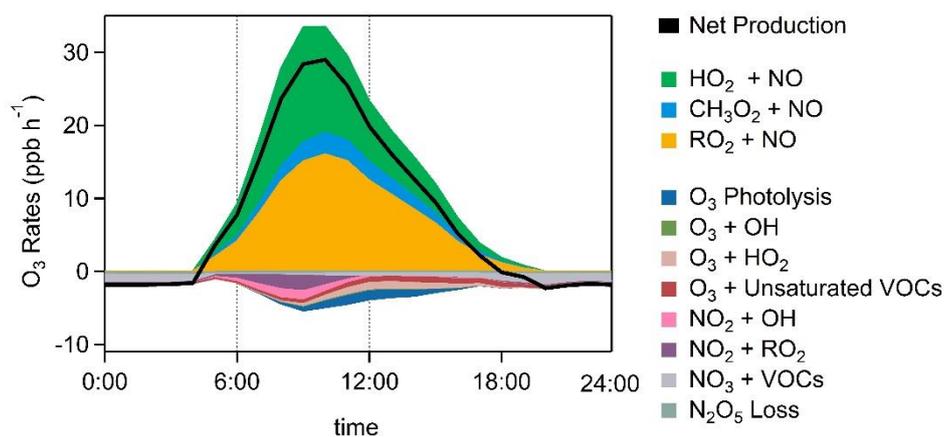
10. Figure 12, daytime average, please specify the exact time span of the hours

**Response:** the time window is 06:00-18:00 local time. We have specified the exact time span

in the revised figure caption.

11. Figure 13, the  $O_3$  loss rate reached up to 20 ppb/h, what are the major reactions for that?

**Response:** we are sorry that the original Figure 13 was wrong. We have corrected the calculation of the  $O_x$  chemical budget, and the revised figure is shown below. Figure 13 has been modified in the revised manuscript.



**Revised Figure 13.** Model-simulated average chemical budgets of  $O_x$  during the selected  $O_3$  episodes.