

Dear Reviewer,

We appreciate your careful consideration of our manuscript. We have carefully responded to all of your **point-by-point** comments and issues and have revised the manuscript accordingly. These revisions are described in detail below.

Ma et al. “Influence of Photochemical Loss of VOCs on Understanding Ozone Formation Mechanism” uses measurements in Beijing to demonstrate how failing to account for oxidation of VOCs between the point of emission and measurement can lead to misinterpretation of the dominant chemical regime for ozone production and a misestimate of the rate of ozone production. The authors use measurements of xylene and ethylbenzene to compute the OH exposure since time of emission, assuming that the concentrations of these species between 5 and 6 AM are a good estimate for their concentrations with zero oxidation. They then use that OH exposure along with rate constants for reaction of other VOCs with OH to back out the “photochemical initial concentrations” (PICs) of VOCs. They compare the net ozone production between the measured and PIC VOC concentrations using a box model with the Master Chemical Mechanism and use another box model with the RACM2 mechanism to examine the dominant ozone production chemical regime with these different VOC concentrations. They conclude that using the measured VOC concentrations underestimates the ozone production rates.

The argument that one must consider the effect of photochemical oxidation of VOCs between source and measurement to accurately determine the best approach to reduce ozone exposure is an important one; however, I do not see that this paper adds much to our understanding of this issue, either generally or specific to Beijing. Additionally, elements of the methodology require further explanation or justification. I will discuss these factors in detail below. Taken together, this paper should be reconsidered after major revision.

**Response:** Thank you for your good comments and suggestions. We will reply your concerns point-by-point below.

## Major comments

1. My largest concern is that it is not clear what this paper adds to our understanding in regards to the effect of VOC degradation on estimated O<sub>3</sub> production rates. This question has previously been addressed by several papers cited in the introduction to this one (e.g. Shao et al., 2011; Gao et al., 2018) as well as others (e.g. Xie et al., 2008; Shao et al., 2009; Li et al., 2015). Near the end of the introduction, this paper states that “it is unclear how the highly reactive VOCs, which [have] degraded during transport from the source to the receptor site, will affect the instantaneous formation process of O<sub>3</sub>.” Yet Li et al. (2015) addresses this in Sect. 3.3. of their paper:

“VOC species may experience photochemical losses from emission sources to receptor sites, which are important for ground-level ozone formation. It is very likely that the OFP [ozone formation potential] is underestimated when using only the observed mixing ratio of ambient VOCs at a receptor site. Therefore, the initial mixing ratios of VOCs must be considered if ozone abatement measures are to be implemented.... We calculated the OFP for the initial VOCs (except carbonyls) to avoid misjudging the role of the major VOC species in ozone formation. The OFPs calculated based on the initial mixing ratio of VOC species differed from those based on observations. The OFPs for total NMHCs (excluding isoprene) increased by 16.09% (from 59.60 to 69.18 ppbv O<sub>3</sub>), 12.06% (from 33.46 to 37.50 ppbv O<sub>3</sub>), and 3.38% (from 68.89 to 71.22 ppbv O<sub>3</sub>) after correction for chemical conversion at GC, QZ, and BJ, respectively.... In this region, the OFPs for trans- 2-butene, cis-2-butene, cis-2-pentene, and isoprene would be underestimated by up to 40% if chemical losses were neglected.”

This analysis by Li et al. (2015) previously showed that not accounting for chemical loss of VOCs will underestimate O<sub>3</sub> production. Replication and confirmation are valuable, but the authors must do a better job placing their paper in the context of earlier work and, especially if replication is the focus, compare their results to previous studies.

**Response:** Thank you for your comments and suggestion. As you mentioned, the influence of photochemical loss of VOCs on OFPs estimation had been discussed based

on the maximum incremental reactivities (MIR) in previous work. However, the application of such calculations using the MIR is restricted to areas or episodes in which the O<sub>3</sub> formation is VOC-sensitive (Carter, 1994). In the troposphere, the sensitivity of ozone formation on NO<sub>x</sub> and VOCs varies greatly. Thus, the non-linear relationship between ozone and VOCs/NO<sub>x</sub> cannot be well elaborated using the MIR method, and a quantitative analysis is necessary for explicitly understanding ozone formation process and mechanisms in the real atmosphere.

In this work, we carried out a thorough analysis on ozone formation using a box model after considering the photochemical loss of VOCs under more realistic atmospheric conditions compared with the MIR method. Our results demonstrated that the ozone sensitivity could be misdiagnosed if one not considering the photochemical loss of VOCs. The contribution of different precursors varied obviously using their initial VOCs concentrations when compared with the observed values, in particular, the contributions of highly reactive alkenes to the RO<sub>2</sub> formation were obviously underestimated using the observed VOCs. In addition, the OH-HO<sub>2</sub> radical cycle was obviously accelerated by the highly reactive alkenes after photochemical loss of VOCs was accounted for. Although this is generally consistent with these previous studies, we discussed this issue based on quantitative analysis including the instantaneous O<sub>3</sub> production rates and the budget of the crucial radicals with the initial concentrations of different precursors. This would provide a technical guidance for regional ozone pollution prevention.

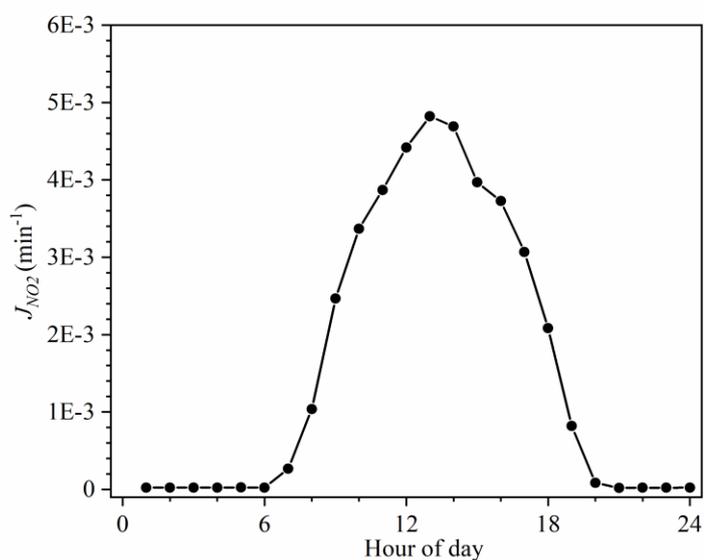
In order to clarify the novelty of this work, we have added more details based on a thorough review of previous work “**In evaluating the importance of initial VOCs to ozone production, Xie et al. (2008) found that the OFP at a Peking University site increased by 70% after accounting for the photochemical loss of VOCs. Li et al. (2015) also showed that the OFPs of total NMHCs (excluding isoprene) increased by 16.1% (from 59.6 to 69.2 ppb O<sub>3</sub>), 12.1% (from 33.5 to 37.5 ppb O<sub>3</sub>), and 3.4% (from 68.9 to**

71.2 ppb O<sub>3</sub>) after correcting for photochemical loss in Gucheng, Quzhou, and Beijing, respectively. Gao et al. (2018) reported that the OFP could be underestimated by 23.4% (62.4 ppb O<sub>3</sub>) in Beijing if the photochemical loss of VOCs is not considered. Zhan et al. (2021) found that based on measured VOCs, the OFP increased from 57.8 ppb to 103.9 ppb using the initial VOCs. All the previous work was based on the maximum incremental reactivities (MIR) method. However, the application of such calculations using the MIR method is restricted to areas or episodes in which O<sub>3</sub> formation is VOC-sensitive (Carter, 1994). In the troposphere, the sensitivity of ozone formation to NO<sub>x</sub> and VOCs varies greatly, as evidenced by the wide range of OFP underestimations from ~3% to 70% in previous work. Thus, the nonlinear relationship between ozone and VOCs/NO<sub>x</sub> cannot be well described using the MIR method, and a quantitative analysis is necessary to explicitly understand the ozone formation process and its mechanisms in the atmosphere.” in lines 78-94 in the revised manuscript.

#### Methodological concerns

2. There are several elements of the methodology that I have concerns about. I will order this section from most to least severe. Choice of initial xylene and ethylbenzene: A key part of this methodology is the use of xylene and ethylbenzene as a chemical clock to compute the integrated OH exposure for all VOCs from emission to measurement. This requires knowing the initial concentrations of xylene and ethylbenzene; for the purposes of this paper, the concentrations between 5 and 6 AM are considered the initial values. This is presumably the last hour before sunrise (and so the last measurement before OH chemistry initiates), but I did not see where the rationale for this selection is given in the paper. The reasoning for that selection should be made clear.

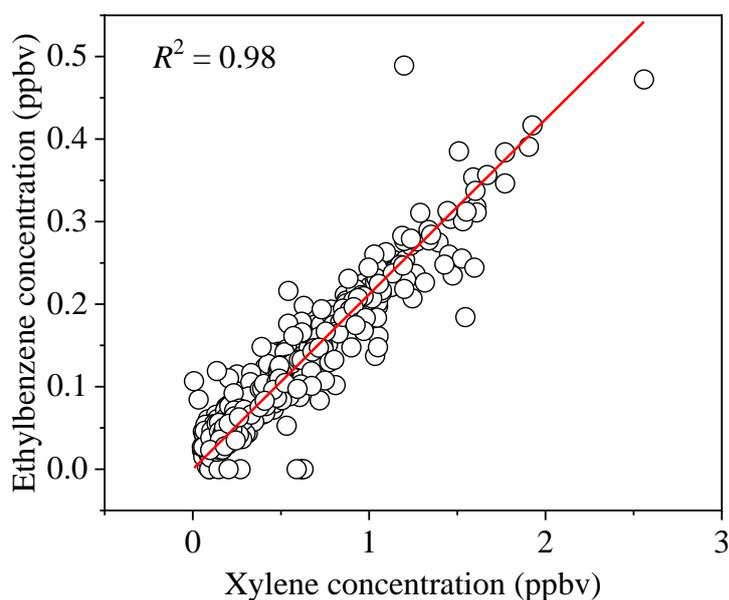
**Response:** Thank you for your good suggestion. Firstly, we choose the initial concentrations of xylene and ethylbenzene based on the diurnal variation of solar irradiation during our observations. As shown in Figure R1, the  $J_{NO_2}$  increased at 7:00 AM, and in order to eliminate the influence of photochemical process, the concentrations at 5:00 and 6:00 AM were set as the initial concentration. In the revised SI, we have added this Figure as Figure S3, and updated the sentence “we chose the mean concentrations of xylene and ethylbenzene at 05:00-06:00 as their initial concentrations before sunrise according to the ambient  $J_{NO_2}$  (Figure S3) to calculate the photochemical loss of OH exposure” in lines 157-160 in the revised manuscript.



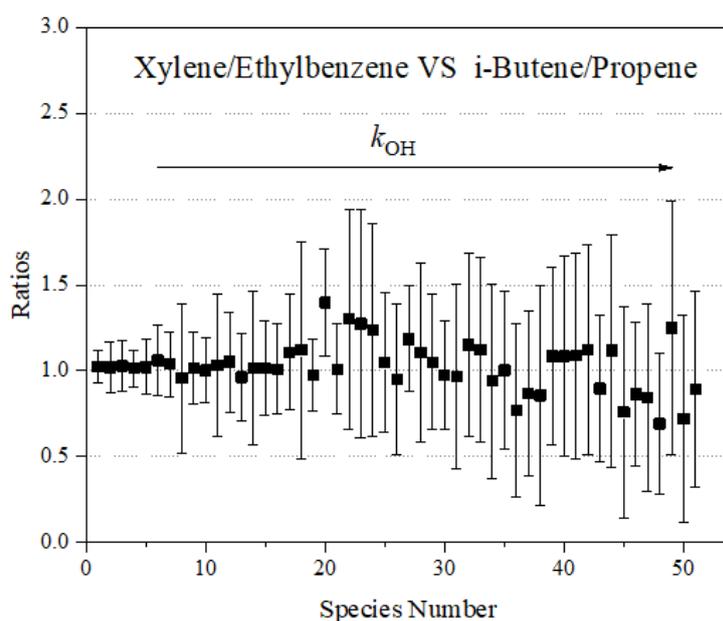
**Figure R1.** The mean diurnal curve of  $J_{NO_2}$ .

3. My larger issue with this approach is that it implicitly assumes that the source of xylene and ethylbenzene remains constant throughout the day. This is a risky assumption: shifts in the wind direction or changes in upwind emissions could alter the source emission ratio of xylene to ethylbenzene throughout the day. I did not see anywhere in the paper where the authors carried out a back trajectory or other source area analysis to determine if the assumption of consistent xylene and ethylbenzene sources throughout the day is correct. Without that analysis, we cannot know if the 5-6 AM xylene and ethylbenzene concentrations are a reasonable approximation of the initial concentrations for all airmasses measured throughout the day.

**Response:** Thank you for your good suggestions. In previous work (Shao et al., 2011; Zhan et al., 2021), it has been justified for selecting the pair of ethylbenzene/xylene as the tracers when one calculating ambient OH exposure in terms of the following rules: 1) the concentrations of xylene and ethylbenzene are well correlated, which indicates that they are simultaneously emitted (Figure R2 and Figure S4); 2) they have different degradation rates in the atmosphere; 3) the calculated PICs are in good agreement with those calculated using other tracers, such as *i*-butene/propene (Figure R3).

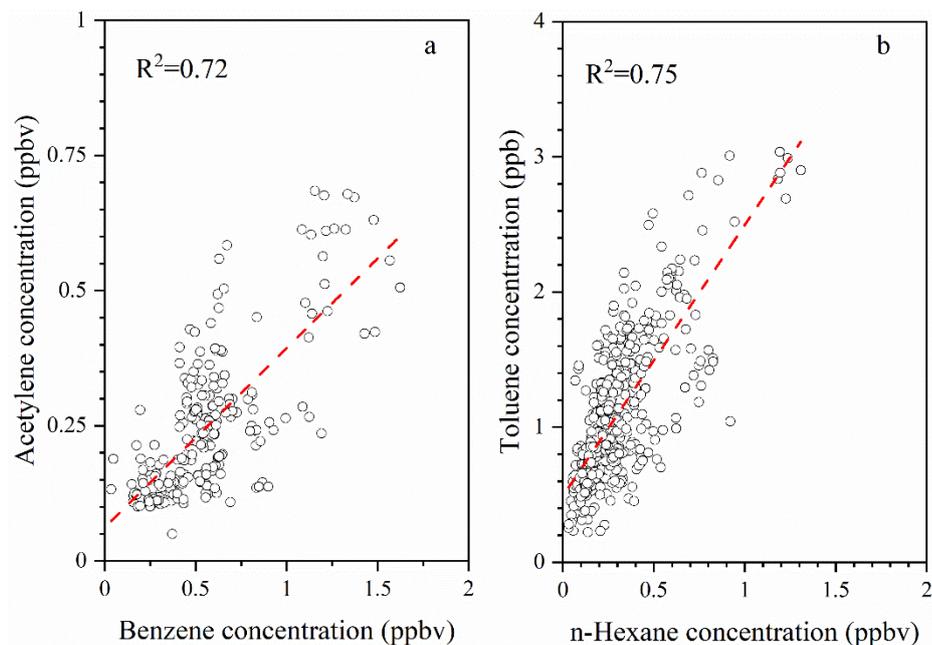


**Figure R2.** The relationship between the concentration of ethylbenzene and xylene.



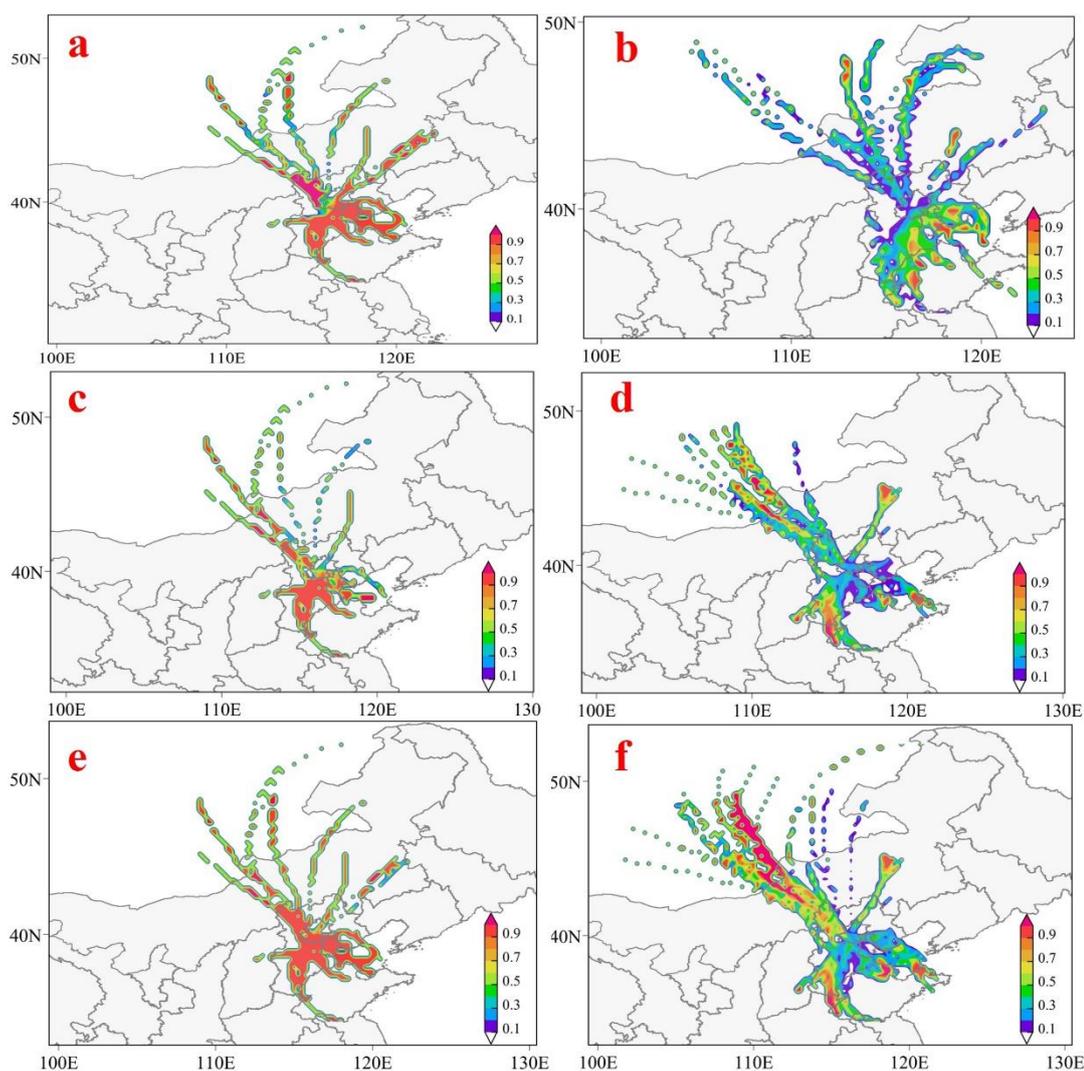
**Figure R3.** Comparison of PICs calculated for xylene/ethylbenzene and i-Butene/Propene. (Error bars are standard deviations.)

In addition, the stability of the emission rates can be evaluated with the ambient ratio for a specific pair of VOCs with similar degradation rate constants (Golden et al., 2000; Jobson et al., 2004), such as benzene *vs* acetylene, trans-2-butene *vs* cis-2-butene, ethene *vs* toluene, and n-hexane *vs* toluene (Shao et al., 2011). Figure R4 (same as Figure S5) shows the correlation between benzene and acetylene, and between n-hexane and toluene during our observations. The linear correlation coefficients ( $R^2$ ) were generally higher than 0.7, which was close to that reported by Shao et al (2011). This means that the emissions of the primary hydrocarbons are relatively constant throughout the day.



**Figure R4.** The relationship between the concentration of benzene vs acetylene and n-hexane vs toluene.

To further check the assumption that the emissions of xylene and ethylbenzene were constant throughout the day, their potential sources have been calculated using a source-receptor model (the potential source contribution function, PSCF) during our observations. As shown in Figure R5 (same as Figure S6), besides the similar trajectories at 5:00 and 6:00 and during the daytime, xylene and ethylbenzene showed the similar distribution. In addition, the ratio of ethylbenzene/xylene at 5:00 and 6:00 were similar to that during the daytime. This means that the wind field was relatively stable during our observations and the emissions of xylene and ethylbenzene were constant throughout the day.



**Figure R5.** The potential source contribution function (PSCF) maps for the ratio of xylene to ethylbenzene (a and b), ethylbenzene (c and d), and xylene (e and f) arriving in the observation site. The figures of a, c and e are the results of 05:00 and 06:00, and the figures of b, d and f are the results during the daytime (07:00-19:00).

In the revised manuscript, we added the sentences “In previous work (Shao et al., 2011; Zhan et al., 2021), the selection of ethylbenzene and xylene as tracers was justified for calculating ambient OH exposure under the following conditions: 1) the concentrations of xylene and ethylbenzene were well correlated (Figure S4), which indicated that they were simultaneously emitted; 2) they had different degradation rates in the atmosphere; and 3) the calculated PICs were in good agreement with those calculated using other tracers, such as i-butene/propene (Zhan et al., 2021). To test the relative constant emission ratio from different sources, we chose benzene vs. acetylene

and n-hexane vs. toluene as references, and the result is shown in Figure S5. These ambient ratios could directly reflect their relative emission rates from sources (Goldan et al., 2000; Jobson et al., 2004). The linear correlation coefficients ( $R^2$ ) were generally higher than 0.7, which were equal to that reported by Shao et al. (2011). To further test the assumption that the emissions of xylene and ethylbenzene were constant throughout the day, their potential sources were calculated using a source-receptor model (the potential source contribution function, PSCF). As shown in Figure S6, xylene and ethylbenzene showed similar distributions. In addition, the ratio of ethylbenzene/xylene at 5:00 and 6:00 was similar to that during the daytime. These results indicated that the emissions of xylene and ethylbenzene were constant throughout the day.” in lines 160-175.

4. Validation of adjusted  $O_3$  production: In the conclusion, the authors claim that, “The radical budget analysis illustrated that the  $O_3$  formation processes between the observed and photochemical initial VOCs showed no significant difference, but the former one underestimated the  $O_3$  production rate obviously” (emphasis added). While I agree in principle that using the observed VOCs underestimates the  $O_3$  production, it is unclear how well the method presented in this paper corrects for that underestimation, as I saw no comparison against any truth metric for  $O_3$  production.

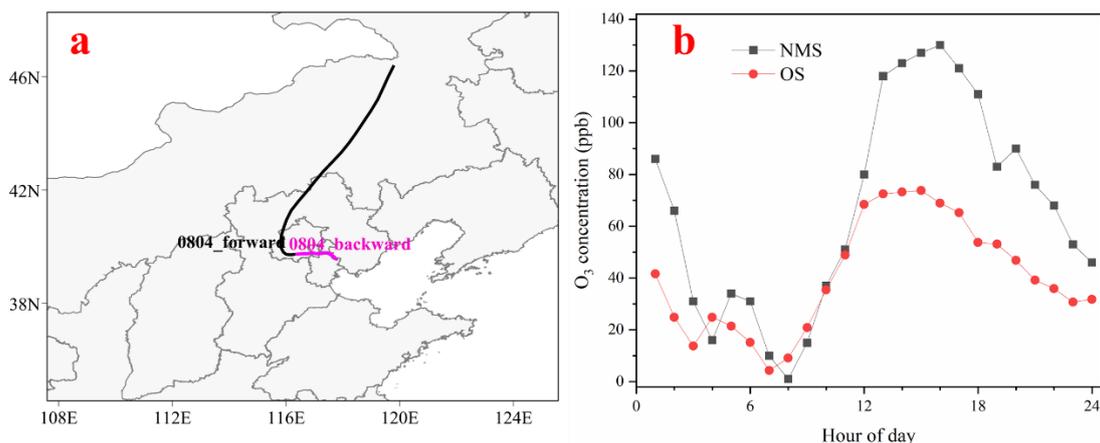
**Response:** Thank you for your comments. We agree with you that it is better to compare the  $O_3$  production with the truth metric for  $O_3$  production. However, it is impossible to directly measure the truth metric for  $O_3$  production in the atmosphere at the present time, subsequently, to answer the question how well the method presented here corrects for that underestimation. On the other hand, we had to constrain the ozone concentrations when simulating the ozone formation process (Lu et al., 2013; Tan et al., 2017). Thus, it was also impossible to directly compare the ozone production between the two scenarios. We compared the net ozone production rates other than ozone production or concentrations in the two scenarios and further compared the ozone production by integrating the net formation rates in the day (7:00-19:00). The calculated ozone production based on the initial VOCs concentrations was  $\sim 36$  ppb day<sup>-1</sup> higher

than that using the measured VOCs concentrations. We think this is reasonable and the best way we can do at the present time. In the revised manuscript, we made it clearer as **It should be pointed out that it is better to compare O<sub>3</sub> production with the true metric for O<sub>3</sub> production. However, it is impossible to directly measure the true metric for O<sub>3</sub> production in the atmosphere at the present time to know how well the method presented here corrects for that underestimation. In addition, the ozone concentrations must be constrained when simulating the ozone formation process (Lu et al., 2013; Tan et al., 2017). Thus, it is impossible to directly compare the ozone production based on PIC-VOCs with that using measured VOCs concentrations. Therefore, we alternatively compared the integrated net ozone production rates rather than ozone production or concentrations between the two scenarios”** in lines 316-324.

5. One method to check the accuracy of the authors' approach would be to use a pair of measurement sites, one upwind and one downwind, with the upwind site measuring O<sub>3</sub> concentration. Combined with a trajectory analysis, one could potentially compute the O<sub>3</sub> production based on the difference in concentrations between the two sites (though mixing may complicate this), and compare that to the modeled O<sub>3</sub> production using observed and PIC VOCs. If an upwind O<sub>3</sub> site is not available, an analysis using  $dO_3/dt$  as in Figure 5, except with independent constraint on the transport of O<sub>3</sub> (perhaps from a regional model or satellite observations) may be another option.

**Response:** Thank you for your good suggestion. We absolutely agree with you that an upwind ozone and VOCs measurement combining with a trajectory analysis might provide an approach to check the accuracy of our results. Alternatively, a transient ozone production rate analysis after subtracting the transport of ozone with a regional model and/or satellite observation may be another option. Unfortunately, neither the upwind measurement nor the regional model simulation was available at the present time. But according to trajectory analysis, we choose 4<sup>th</sup> August as the case to

explore the influence of the transport of ozone on one downwind site. As showed in Figure R6 (same as Figure S12), the mean ozone concentration of the downwind site (national monitoring station, NMS) was  $27.6 \pm 21.8$  ppb day<sup>-1</sup> higher than the observation site (OS), slightly lower than the difference ( $\sim 36$  ppb day<sup>-1</sup>) between PIC-VOCs and observed VOCs, which indirectly supported the accuracy of our results. We added the corresponding analysis in the revised manuscript in lines 324-334 “An upwind O<sub>3</sub> and VOCs measurement combined with a trajectory analysis might provide an approach for checking the accuracy of our results. Alternatively, conducting a transient O<sub>3</sub> production rate analysis after subtracting the transport of O<sub>3</sub> with a regional model and/or satellite observation might be another option. Unfortunately, neither the upwind measurement nor the regional model simulation was available at the time of our study. To further check the accuracy of our results, we chose August 4<sup>th</sup> as a test case to explore the influence of the transport of ozone on a downwind site based on the trajectory analysis. As shown in Figure S12, the mean ozone concentration of the downwind site (national monitoring station, NMS) was  $27.6 \pm 21.9$  ppb day<sup>-1</sup> higher than that of the observation site (OS), which was slightly less than the difference ( $\sim 36$  ppb day<sup>-1</sup>) between PIC-VOCs and observed VOCs and indirectly rationalized our results.”.

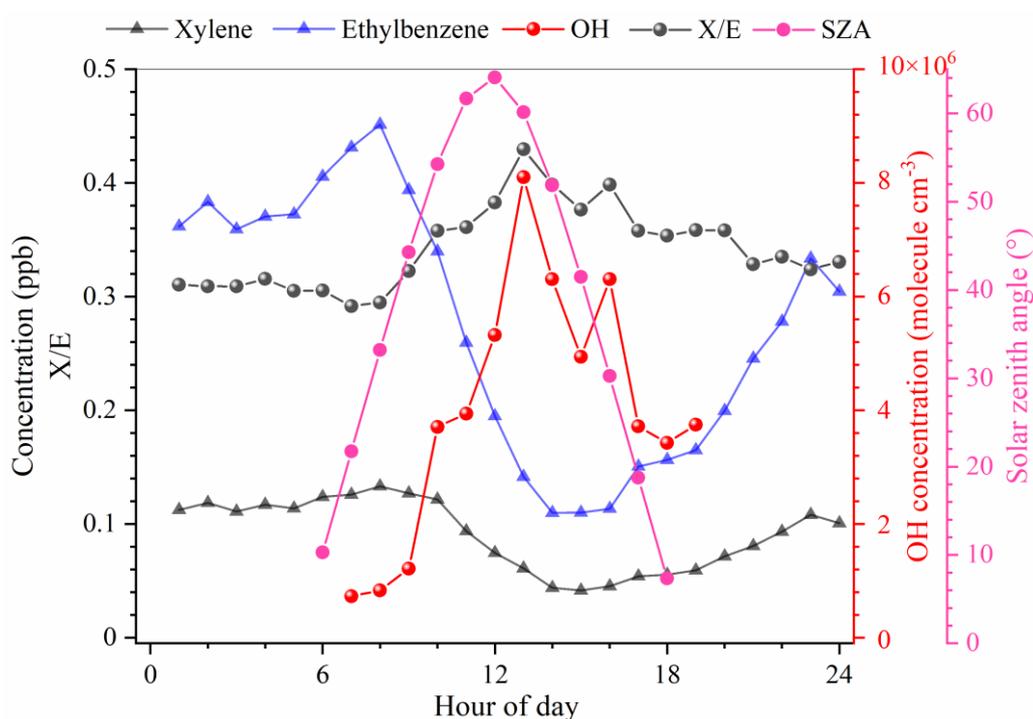


**Figure R6.** The wind direction at the observation site on 4<sup>th</sup> Aug (a, backward and forward meaning upwind and downwind, respectively) and the diurnal variation of ozone concentration at observation site (OS) and one downwind site (national monitoring station (NMS)).

6. VOC correction: In Figure 1, the difference between the observed and “photochemical initial concentration” (PIC) VOCs is zero before 6a and after 7p (19:00). Between 6a and 7p, the offset between the observed and PIC VOC concentrations seems almost (but not quite) constant. What seems particularly odd is how the observed-PIC difference jumps from nothing to essentially its maximum value between 5a and 6a, then likewise drops instantaneously from its maximum value to zero between 7p and 8p. I would expect the transition to be more gradual, with photolysis (and therefore OH concentrations) being less in the hour immediately following sunrise than later in the morning (and vice versa at night). It would be helpful if the authors provided a timeseries (at sub-hourly resolution) of the concentration of xylene and ethylbenzene, their ratio, the OH exposure derived from these quantities, and the solar zenith angle, to demonstrate how the OH exposure correction changes with time of day.

**Response:** Thank you for your comments and good suggestion. The transition of the initial VOCs should gradually increase with photolysis as you pointed out. Figure R7 (same as FigureS7) shows the mean diurnal curves of the concentrations of xylene and ethylbenzene, their ratio, the OH concentration and the solar zenith angle. The variation of solar zenith angle was similar to that of  $J_{NO2}$  (Figure R1). The OH

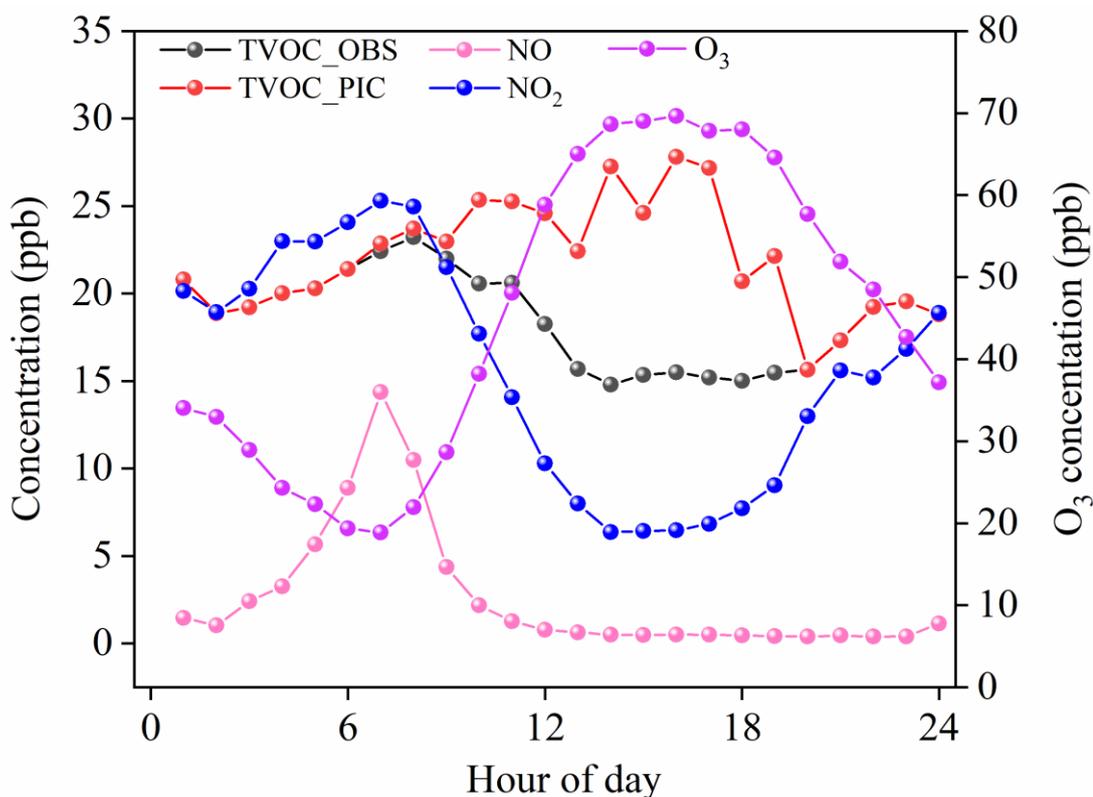
concentration was from 0.82 to  $8.1 \times 10^6$  ( $4.3 \pm 1.9 \times 10^6$ ), the ratio of xylene to ethylbenzene increased gradually (07:00~12:00). In the revised manuscript in lines 177-181, we added the sentences “The ratio of xylene to ethylbenzene and the OH exposure concentration are shown in Figure S7. The results showed that the ratio of xylene to ethylbenzene increased gradually (07:00~12:00), which is consistent with the trend of xylene and ethylbenzene. The OH exposure was from 0.82 to  $8.1 \times 10^6$  molecule  $\text{cm}^{-3}$  h, with a mean daytime value of  $4.3 \pm 1.9 \times 10^6$  molecules  $\text{cm}^{-3}$  h.”.



**Figure R7.** The mean diurnal curves of the concentration of xylene and ethylbenzene, their ratio, the OH exposure concentration (molecule  $\text{cm}^{-3}$ ), and solar zenith angle.

We double checked the PIC concentrations and the related dataset from 07:00 to 19:00 in Figure 1. We are sorry for a stupid mistake when drawing Figure 1. We wrongly added the data of 05:00 and 06:00 twice when calculating PICs of VOCs from 07:00 to 12:00, thus leading to the sharp increase in the early morning (07:00-10:00). The simulation process using the PIC-VOCs is correct. And we have corrected the Figure 1 (Figure R8) and the updated the sentences in lines 259-265 in the revised manuscript

“However, the photochemical initial concentrations (PICs) of TVOCs, which varied from 2.2 to 27.8 ppb with a mean value of  $24.5 \pm 2.1$  ppb, showed a different diurnal curve compared with the observed concentrations. It slightly increased from 07:00 to 14:00, which was similar to the diurnal variation of VOCs in previous work (Zhan et al., 2021). The average PIC-VOCs was  $6.9 \pm 0.5$  ppb higher than the observed concentration of TVOCs, indicating an underestimated contribution of the local photochemistry of VOCs to O<sub>3</sub> and organic aerosol formation.”



**Figure R8.** Overview of average diurnal variations of O<sub>3</sub>, NO<sub>x</sub>, and TVOC. The data represent measured results, except for those of the TVOC\_PIC, which are calculated based on OH radical exposure. The data range is August 1-28, 2019.

7. Ozone production and loss metrics: Please discuss for Eq. 3 how alkyl nitrate formation is treated; is  $k_{RO_2+NO}$  the rate constants for only  $RO_2 + NO$  reactions that produce RO and NO<sub>2</sub>? If  $k_{RO_2+NO}$  is the rate for all  $RO_2 + NO$  reactions, then the alkyl

nitrate branching ratio must be accounted for.

**Response:** Thank you for your comments. We agree with you that the reaction between RO<sub>2</sub> and NO can produce both RO and alkyl nitrate. The branching ratio was actually accounted for in the model. For example,



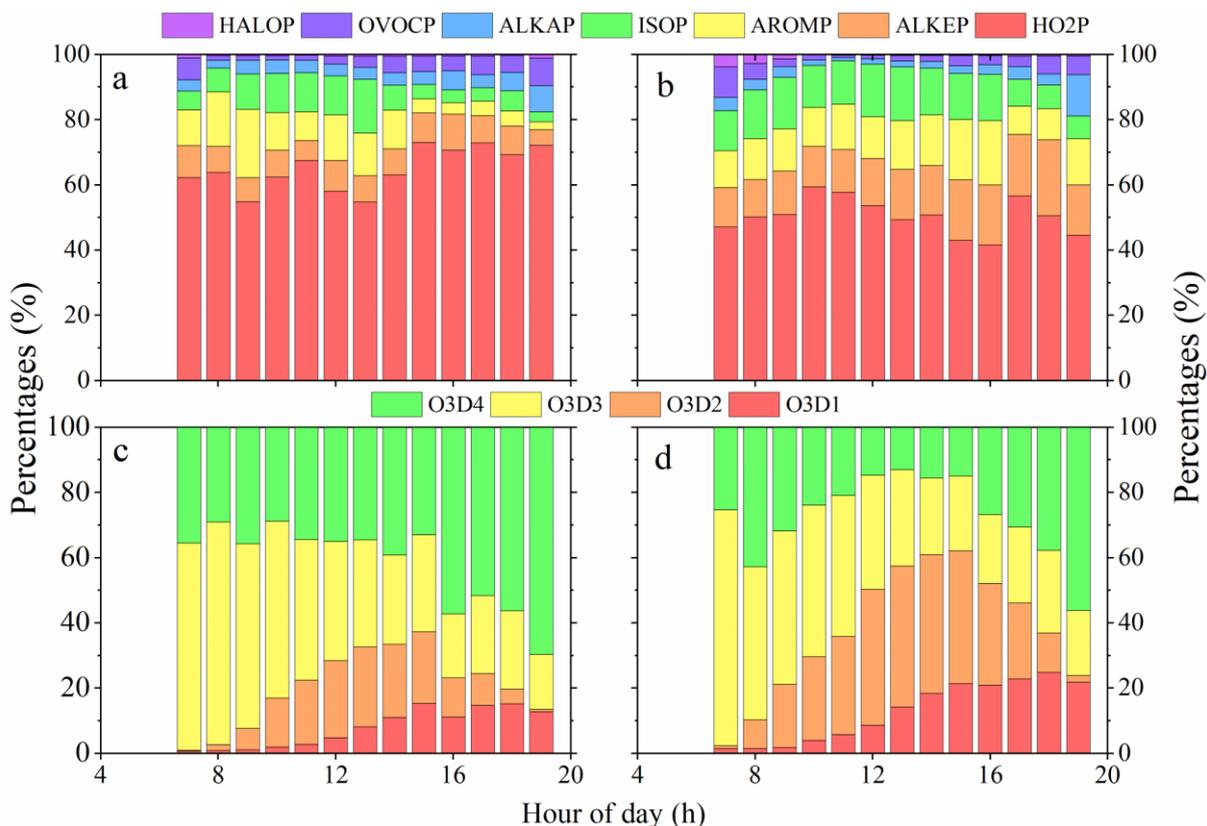
where, TEMP is the temperature, and the numbers of 0.999 and 0.001 are the branching ratio for Eq. R1 and R2, respectively.

When calculating the ozone production and loss in Eq.3, we just marked the RO path in the master chemical mechanism, such as Eq. R1, and excluded the alkyl nitrate branch (Eq. R2). Therefore, the  $k_{\text{RO}_2+\text{NO}}$  in Eq. 3 is indeed the reaction rate constant between RO<sub>2</sub> and NO that produce the RO and NO<sub>2</sub>. In the revised manuscript, we clearly clarified it “ $k_{\text{HO}_2+\text{NO}}$  is the second reaction rate between HO<sub>2</sub> and NO; and  $k_{\text{RO}_2+\text{NO}}$  is the second reaction rate for the reaction between RO<sub>2</sub> and NO, which only produces RO and NO<sub>2</sub>.” in lines 214-215.

8. Relatedly, in Figure 3, a comparison of panels (c) and (d) appears to indicate that the loss of ozone via reaction of O1D with H<sub>2</sub>O increases when using PIC VOCs rather than measured. Please elaborate why this is, is this just because there is more O<sub>3</sub> (and so more O1D) in the model with PIC VOCs, and so the rate increases even through the amount of H<sub>2</sub>O remains constant? If so, it might help to include a companion figure to Figure 3 in the supplement that shows P(O<sub>3</sub>) and L(O<sub>3</sub>) as percentages of O<sub>3</sub> production/loss to help the reader understand the relative change in loss processes as well.

**Response:** Thank you for your comments and good suggestion. Yes, the loss rate of ozone via reaction of O1D with H<sub>2</sub>O ( $2.2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298K, Atkinson et al., 2004) is higher when using the PIC-VOCs than that between ozone and alkenes ( $1.27 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298K, Atkinson et al., 1994). Therefore, photolysis of ozone contributes more O1D, leading to enhanced consumption of O<sub>3</sub> by H<sub>2</sub>O. Figure

R9 shows the percentages of different paths of P(O<sub>3</sub>) and L(O<sub>3</sub>). The relative contributions of the reactions between O<sub>3</sub> and alkenes (O1D3) and between NO<sub>2</sub> and OH (O1D4) to O<sub>3</sub> loss decrease calculated on the basis of the PIC-VOCs when compared with the measured VOCs, while it increases obviously for other two paths, i.e. O3D1 and O3O2.



**Figure R9.** The percentages of different ozone production and loss rate (observed VOCs in a and c, and PIC-VOCs in b and d). The upper and lower panels present the percentages of different ozone production and loss rate, respectively.

We added the Figure R9 as Figure S13 in the SI. In the revised manuscript in [lines 345-349](#), we added a short paragraph “[Figure S13 shows the percentages of the different paths of P\(O<sub>3</sub>\) and L\(O<sub>3</sub>\). The relative contributions of the reactions between O<sub>3</sub> and alkenes \(O1D3\) and between NO<sub>2</sub> and OH \(O1D4\) to the O<sub>3</sub> sinks decreased when calculated based on PIC-VOCs compared with those of the measured VOCs, while they obviously increased for the other two paths, i.e., O3D1 and O3O2.](#)”.

## Minor comments

1. The argument made in lines 69-75 of the introduction about the different mixing ratios of VOCs at the source vs. measurement site is confusing on a first read because it is not clear that the scenario which applies here is where the source one is attempting to control with policy is significantly upwind of the measurement site. If we were considering a source (e.g. traffic) which is closely clustered around the measurement site, then the VOCs measured at the site will be the correct concentrations to consider for O<sub>3</sub> production.

**Response:** Thank you for good comments. We agree with you that the VOCs measured at the site will be the correct concentrations to consider for O<sub>3</sub> production if we are considering a source (e.g. traffic) which is closely clustered around the measurement site. However, on a regional or urban scale, our argument is reasonable. In the revised manuscript, we have made it clearer “**The mixing ratios of VOCs observed at a sampling site are actually the residues of VOCs from emissions due to the photochemical loss during transport from the source site to the receptor site. If photochemically consumed VOCs are not considered, the O<sub>3</sub> formation sensitivity and net O<sub>3</sub> production may be misunderstood, and subsequent policymaking on O<sub>3</sub> pollution prevention at regional or urban scales may be misguided. Thus, the photochemical age-based approach has been applied to evaluate the effect of photochemical processes on VOC measurements (Shao et al., 2011)**” in lines 69-75.

2. It is unclear whether Figure 1 and (to a lesser extent) Figure 3 are for one specific day or the entire campaign. For these figures, please specify the time period considered (since Figure 5 is specific to one day).

**Response:** Thank you for your suggestion. Both Figure 1 and Figure 3 are for the entire campaign. In the captions of Figures 1 and 3 in the revised manuscript, we clarified it as “**The data range is August 1-28, 2019**”.

3. For Figure 1, specify which series are measurements and which are calculated. (I assume all but the TVOC PIC series are measurements, but please be explicit.)

**Response:** Thank you. In the revised manuscript, we added a short sentence “**The data represent measured results, except for those of the TVOC\_PIC, which are calculated based on OH radical exposure.**” in the caption of Figure 1.

4. For Figure 2, define specific times (i.e. “8 AM” or “11 AM to 1 PM”) rather than “morning” and “noon” so that we can compare to Figure 1. Also, line 278 seems to imply that the “noon” points are actually 15:00? That is confusing.

**Response:** Thank you. In the revised manuscript, we have updated the caption of Figure 2 “The pentagons and stars indicate the status in the morning (09:00-10:00) and at noon (14:00-15:00), respectively.” In lines 276-279 in the revised manuscript, we also updated the specific time “The black full star and pentagon denote the observed concentrations of NO<sub>x</sub> and VOCs in the morning (09:00-10:00) and at noon (14:00-15:00), respectively, while the blue symbols are the corresponding values of PICs”.

5. Please explain in the caption what the percentages in Figure 4 represent; I only saw a description of the other numbers as production rates in ppb h<sup>-1</sup>. In general, the discussion of the radical chain on lines 362-387 is pretty dense and difficult to follow, but I cannot give any suggestions to improve it without understanding what all the elements in Figure 4 are.

**Response:** Thank you for your good suggestion. The percentages in the box are relative contributions of different reaction paths to the production rate of corresponding radicals in Figure 4. In the revised manuscript, we have updated the sentence in the caption of Figure 4 “**The numbers or percentages outside and inside the brackets are the average formation rates (ppb h<sup>-1</sup>) or relative contributions of the corresponding reaction path based on observed VOCs and PIC-VOCs, respectively, to a specific radical.**”.

In lines 365-390 in the revised manuscript, we have updated this paragraph “The budget of OH-HO<sub>2</sub>-RO<sub>2</sub> radicals was further analyzed to understand the photochemical O<sub>3</sub> formation process. **The comparison of the radical budget derived from the observed**

and PIC-VOCs is shown in Figure 4. The radical cycles are divided into radical sources (green boxes), radical sinks (black boxes), radical propagations (red circles) and equilibria between radical and reservoir species (yellow boxes). The numbers or percentages are the average formation rates ( $\text{ppb h}^{-1}$ ) or relative contributions of the corresponding reaction path based on the observed VOCs (outside the brackets) and the PIC-VOCs (inside the brackets) to a certain radical. The relative contributions of different radical paths based on the observed VOCs (outside the brackets) were comparable with those reported in Beijing, Shanghai, and Guangzhou (Tan et al., 2019), while variations were observed for some reaction paths based on the PIC-VOCs. For example, the reaction between ozone and alkenes based on initial VOC concentrations (percentages inside the brackets) contributed more to OH (from 7% to 21%) and HO<sub>2</sub> radical production (from 6% to 12%), while photolysis of HONO and HCHO contributed less to the production of OH (from 76% to 60%) and HO<sub>2</sub> radicals (from 44% to 40%), respectively. Other radical sources were consistent between the two scenarios. Interestingly, the average formation rates of OH, HO<sub>2</sub> and RO<sub>2</sub> radicals derived from the PIC-VOCs were obviously higher than those from the observed VOCs. In particular, the oxidation of NO by RO<sub>2</sub> and HO<sub>2</sub> increased by 1.6 and 1.3  $\text{ppb h}^{-1}$ , respectively. The enhanced oxidation rate of NO was equal to the increase in the average F(O<sub>3</sub>) in the analysis process above. This meant that the radical propagation of OH-RO<sub>2</sub>-HO<sub>2</sub> sped up in the case of PIC-VOCs, subsequently accelerating the chemical loop of NO-NO<sub>2</sub>-O<sub>3</sub>. For the radical sinks and equilibria related to HNO<sub>4</sub>, RONO<sub>2</sub> and PAN, the values were basically comparable between the two scenarios. In addition, the

O<sub>3</sub> formation from the RO<sub>2</sub> path increased by 4.1% (from 39.5% to 43.6%) in the simulation using the PIC-VOCs compared with the observed VOCs. The above budget analysis explained the observed increases in F(O<sub>3</sub>) (~3 ppb h<sup>-1</sup>), which were mainly driven by the reaction of missed reactive VOCs, such as alkenes, with O<sub>3</sub>.”.

## Summary

While this paper is a fair study of how one might account for degradation of VOCs between sources and measurements in order to formulate better approaches to controlling O<sub>3</sub> production, there have been a number of earlier studies looking at this problem in Beijing. In my opinion, in order for a revision to be considered for publication, the authors must revise the paper to clarify what new information their work adds compared to the previous studies or refocus the paper as a replication study or an update to more recent times. In this second case, the revision should include a thorough comparison with previous studies of this effect in the Beijing area.

**Response:** Thank you for your comment. We have responded all your good comments and suggestions aforementioned. In conclusion, we quantitatively discussed the influence of VOCs degradation between sources and measurements on understanding ozone pollution based on OBM simulations. When comparing with these previous studies estimating OFP with the MIR method, this study has accounted for the non-linear relationship of O<sub>3</sub> formation to VOCs and NO<sub>x</sub>. In addition, we provide more details about this issue based on budget analysis of the crucial radicals related to O<sub>3</sub> formation. An underestimation should be about 3 ppb h<sup>-1</sup> or 36 ppb day<sup>-1</sup> for O<sub>3</sub> production rate, which is mainly driven by the reaction between the missed reactive VOCs, such as alkenes, with O<sub>3</sub> during our observation. In addition, highly reactive alkenes by the photochemical oxidation accelerated the OH and HO<sub>2</sub> radical cycle.

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