

1 Dear Reviewer,

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

5

6 **Reviewer #1**

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

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

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

29

30

31 **Major comments**

32 1. My largest concern is that it is not clear what this paper adds to our understanding in regards
33 to the effect of VOC degradation on estimated O₃ production rates. This question has previous
34 been addressed by several papers cited in the introduction to this one (e.g. Shao et al., 2011;
35 Gao et al., 2018) as well as others (e.g. Xie et al., 2008; Shao et al., 2009; Li et al., 2015). Near
36 the end of the introduction, this paper states that “it is unclear how the highly reactive VOCs,
37 which [have] degraded during transport from the source to the receptor site, will affect the
38 instantaneous formation process of O₃.” Yet Li et al. (2015) addresses this in Sect. 3.3. of their
39 paper:

40 “VOC species may experience photochemical losses from emission sources to receptor
41 sites, which are important for ground-level ozone formation. It is very likely that the OFP
42 [ozone formation potential] is underestimated when using only the observed mixing ratio of
43 ambient VOCs at a receptor site. Therefore, the initial mixing ratios of VOCs must be
44 considered if ozone abatement measures are to be implemented.... We calculated the OFP for
45 the initial VOCs (except carbonyls) to avoid misjudging the role of the major VOC species
46 in ozone formation. The OFPs calculated based on the initial mixing ratio of VOC species
47 differed from those based on observations. The OFPs for total NMHCs (excluding isoprene)
48 increased by 16.09% (from 59.60 to 69.18 ppbv O₃), 12.06% (from 33.46 to 37.50 ppbv O₃),
49 and 3.38% (from 68.89 to 71.22 ppbv O₃) after correction for chemical conversion at GC,
50 QZ, and BJ, respectively.... In this region, the OFPs for trans- 2-butene, cis-2-butene, cis-2-
51 pentene, and isoprene would be underestimated by up to 40% if chemical losses were
52 neglected.”

53

54 This analysis by Li et al. (2015) previously showed that not accounting for chemical loss of
55 VOCs will underestimate O₃ production. Replication and confirmation are valuable, but the
56 authors must do a better job placing their paper in the context of earlier work and, especially if
57 replication is the focus, compare their results to previous studies.

58 **Response:** Thank you for your comments and suggestion. As you mentioned, the
59 influence of photochemical loss of VOCs on OFPs estimation had been discussed based on the
60 maximum incremental reactivities (MIR) in previous work. However, the application of such

61 calculations using the MIR is restricted to areas or episodes in which the O₃ formation is VOC-
62 sensitive (Carter, 1994). In the troposphere, the sensitivity of ozone formation on NO_x and
63 VOCs varies greatly. Thus, the non-linear relationship between ozone and VOCs/NO_x cannot
64 be well elaborated using the MIR method, and a quantitative analysis is necessary for explicitly
65 understanding ozone formation process and mechanisms in the real atmosphere.

66 In this work, we carried out a thorough analysis on ozone formation using a box model
67 after considering the photochemical loss of VOCs under more realistic atmospheric conditions
68 compared with the MIR method. Our results demonstrated that the ozone sensitivity could be
69 misdiagnosed if one not considering the photochemical loss of VOCs. The contribution of
70 different precursors varied obviously using their initial VOCs concentrations when compared
71 with the observed values, in particular, the contributions of highly reactive alkenes to the RO₂
72 formation were obviously underestimated using the observed VOCs. In addition, the OH-HO₂
73 radical cycle was obviously accelerated by the highly reactive alkenes after photochemical loss
74 of VOCs was accounted for. Although this is generally consistent with these previous studies,
75 we discussed this issue based on quantitative analysis including the instantaneous O₃
76 production rates and the budget of the crucial radicals with the initial concentrations of different
77 precursors. This would provide a technical guidance for regional ozone pollution prevention.

78 In order to clarify the novelty of this work, we have added more details based on a
79 thorough review of previous work “In evaluating the importance of initial VOCs to ozone
80 production, Xie et al. (2008) found that the OFP at a Peking University site increased by 70%
81 after accounting for the photochemical loss of VOCs. Li et al. (2015) also showed that the
82 OFPs of total NMHCs (excluding isoprene) increased by 16.1% (from 59.6 to 69.2 ppb O₃),
83 12.1% (from 33.5 to 37.5 ppb O₃), and 3.4% (from 68.9 to 71.2 ppb O₃) after correcting for
84 photochemical loss in Gucheng, Quzhou, and Beijing, respectively. Gao et al. (2018) reported
85 that the OFP could be underestimated by 23.4% (62.4 ppb O₃) in Beijing if the photochemical
86 loss of VOCs is not considered. Zhan et al. (2021) found that based on measured VOCs, the

87 OFP increased from 57.8 ppb to 103.9 ppb using the initial VOCs. All the previous work was
88 based on the maximum incremental reactivities (MIR) method. However, the application of
89 such calculations using the MIR method is restricted to areas or episodes in which O₃ formation
90 is VOC-sensitive (Carter, 1994). In the troposphere, the sensitivity of ozone formation to NO_x
91 and VOCs varies greatly, as evidenced by the wide range of OFP underestimations from ~3%
92 to 70% in previous work. Thus, the nonlinear relationship between ozone and VOCs/NO_x
93 cannot be well described using the MIR method, and a quantitative analysis is necessary to
94 explicitly understand the ozone formation process and its mechanisms in the atmosphere.” in
95 lines 78-94 in the revised manuscript.

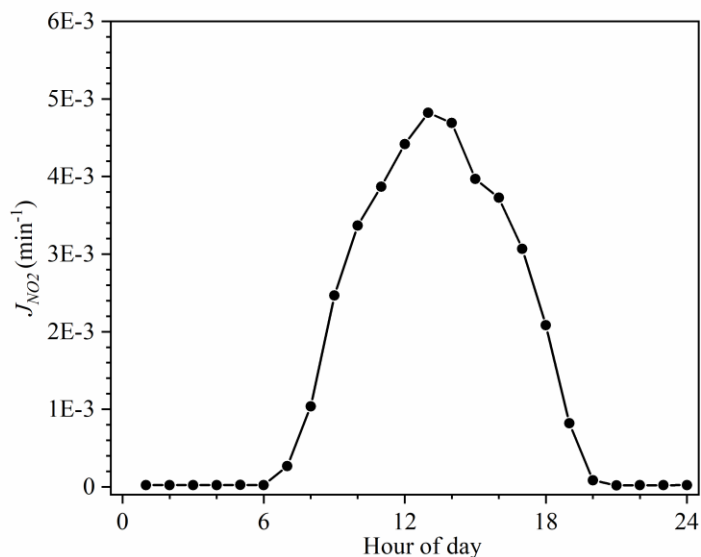
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97 Methodological concerns

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

107 **Response:** Thank you for your good suggestion. Firstly, we choose the initial
108 concentrations of xylene and ethylbenzene based on the diurnal variation of solar irradiation
109 during our observations. As shown in Figure R1, the J_{NO_2} increased at 7:00 AM, and in order
110 to eliminate the influence of photochemical process, the concentrations at 5:00 and 6:00 AM
111 were set as the initial concentration. In the revised SI, we have added this Figure as Figure S3,
112 and updated the sentence “we chose the mean concentrations of xylene and ethylbenzene at
113 05:00-06:00 as their initial concentrations before sunrise according to the ambient J_{NO_2} (Figure

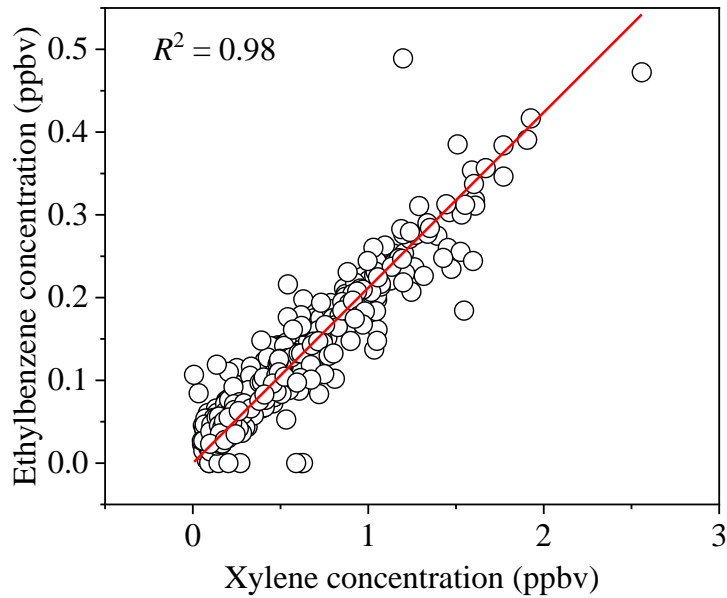
114 S3) to calculate the photochemical loss of OH exposure” in lines 157-160 in the revised
115 manuscript.



116
117 **Figure R1.** The mean diurnal curve of J_{NO_2} .

118
119 3. My larger issue with this approach is that it implicitly assumes that the source of xylene and
120 ethylbenzene remains constant throughout the day. This is a risky assumption: shifts in the wind
121 direction or changes in upwind emissions could alter the source emission ratio of xylene to
122 ethylbenzene throughout the day. I did not see anywhere in the paper where the authors carried
123 out a back trajectory or other source area analysis to determine if the assumption of consistent
124 xylene and ethylbenzene sources throughout the day is correct. Without that analysis, we cannot
125 know if the 5-6 AM xylene and ethylbenzene concentrations are a reasonable approximation
126 of the initial concentrations for all airmasses measured throughout the day.

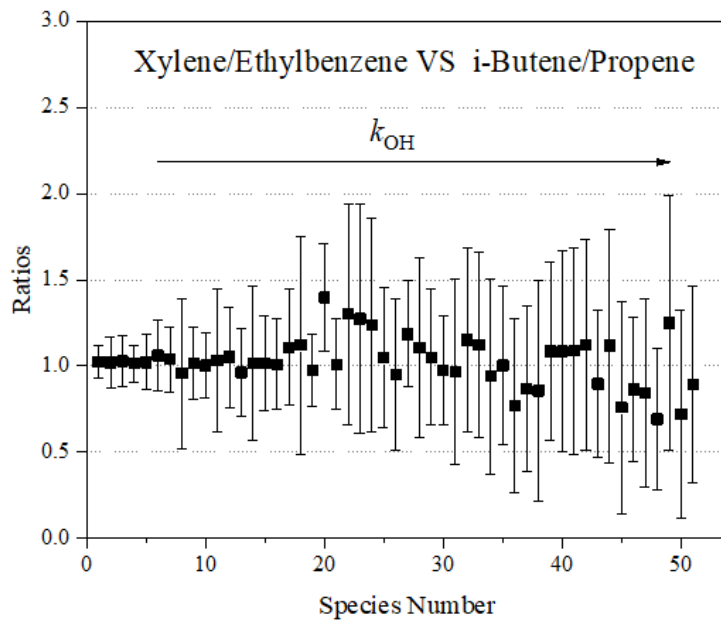
127 **Response:** Thank you for your good suggestions. In previous work (Shao et al., 2011;
128 Zhan et al., 2021), it has been justified for selecting the pair of ethylbenzene/xylene as the
129 tracers when one calculating ambient OH exposure in terms of the following rules: 1) the
130 concentrations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



134

135

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



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137

Figure R3. Comparison of PICs calculated for xylene/ethylbenzene and i-Butene/Propene.

138

(Error bars are standard deviations.)

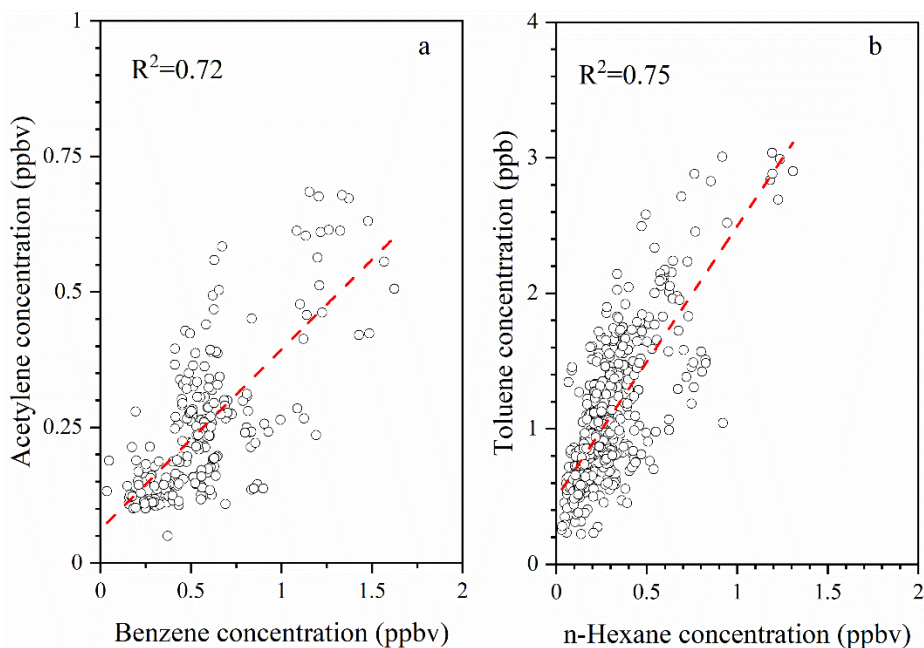
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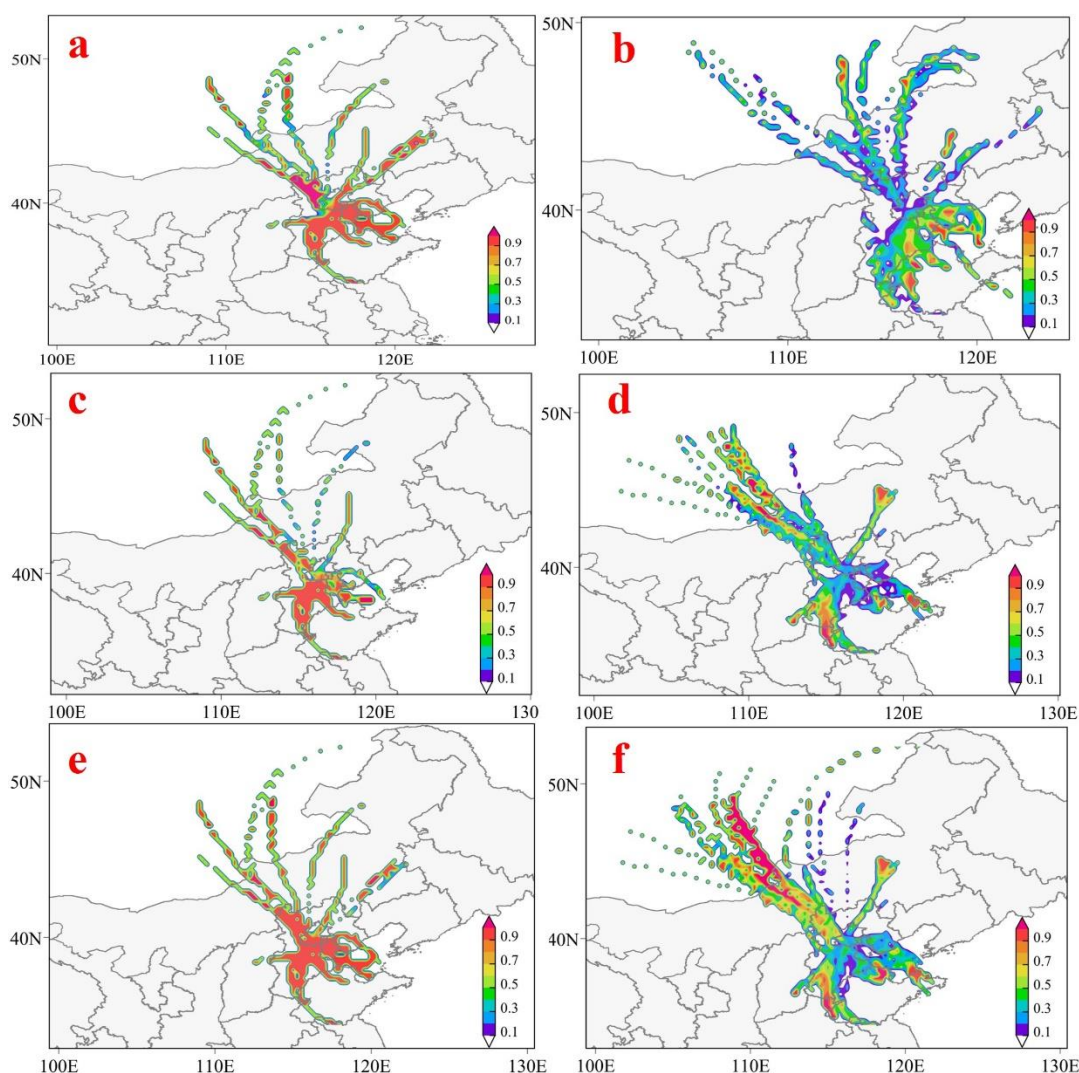
In addition, the stability of the emission rates can be evaluated with the ambient ratio for a specific pair of VOCs with similar degradation rate constants (Golden et al., 2000; Jobson et al., 2004), such as benzene vs acetylene, trans-2-butene vs cis-2-butene, ethene vs toluene, and

142 n-hexane vs toluene (Shao et al., 2011). Figure R4 (same as Figure S5) shows the correlation
143 between benzene and acetylene, and between n-hexane and toluene during our observations.
144 The linear correlation coefficients (R^2) were generally higher than 0.7, which was close to that
145 reported by Shao et al (2011). This means that the emissions of the primary hydrocarbons are
146 relatively constant throughout the day.



147
148 **Figure R4.** The relationship between the concentration of benzene vs acetylene and n-
149 hexane vs toluene.

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



158
 159 **Figure R5.** The potential source contribution function (PSCF) maps for the ratio of xylene to
 160 ethylbenzene (a and b), ethylbenzene (c and d), and xylene (e and f) arriving in the observation
 161 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
 162 are the results during the daytime (07:00-19:00).

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

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

180

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

188 **Response:** Thank you for your comments. We agree with you that it is better to compare the
189 O_3 production with the truth metric for O_3 production. However, it is impossible to directly
190 measure the truth metric for O_3 production in the atmosphere at the present time, subsequently,
191 to answer the question how well the method presented here corrects for that underestimation.
192 On the other hand, we had to constrain the ozone concentrations when simulating the ozone
193 formation process (Lu et al., 2013; Tan et al., 2017). Thus, it was also impossible to directly
194 compare the ozone production between the two scenarios. We compared the net ozone
195 production rates other than ozone production or concentrations in the two scenarios and further
196 compared the ozone production by integrating the net formation rates in the day (7:00-19:00).
197 The calculated ozone production based on the initial VOCs concentrations was ~ 36 ppb day⁻¹
198 higher than that using the measured VOCs concentrations. We think this is reasonable and the
199 best way we can do at the present time. In the revised manuscript, we made it clearer as **It**
200 **should be pointed out that it is better to compare O_3 production with the true metric for O_3**

201 production. However, it is impossible to directly measure the true metric for O₃ production in
202 the atmosphere at the present time to know how well the method presented here corrects for
203 that underestimation. In addition, the ozone concentrations must be constrained when
204 simulating the ozone formation process (Lu et al., 2013; Tan et al., 2017). Thus, it is impossible
205 to directly compare the ozone production based on PIC-VOCs with that using measured VOCs
206 concentrations. Therefore, we alternatively compared the integrated net ozone production rates
207 rather than ozone production or concentrations between the two scenarios” in lines 316-324.

208

209 5. One method to check the accuracy of the authors’ approach would be to use a pair of
210 measurement sites, one upwind and one downwind, with the upwind site measuring O₃
211 concentration. Combined with a trajectory analysis, one could potentially compute the O₃
212 production based on the difference in concentrations between the two sites (though mixing may
213 complicate this), and compare that to the modeled O₃ production using observed and PIC VOCs.
214 If an upwind O₃ site is not available, an analysis using dOx/dt as in Figure 5, except with
215 independent constraint on the transport of O₃ (perhaps from a regional model or satellite
216 observations) may be another option.

217 **Response:** Thank you for your good suggestion. We absolutely agree with you that an
218 upwind ozone and VOCs measurement combining with a trajectory analysis might provide an
219 approach to check the accuracy of our results. Alternatively, a transient ozone production rate
220 analysis after subtracting the transport of ozone with a regional model and/or satellite
221 observation may be another option. Unfortunately, neither the upwind measurement nor the
222 regional model simulation was available at the present time. But according to trajectory
223 analysis, we choose 4th August as the case to explore the influence of the transport of ozone on
224 one downwind site. As showed in Figure R6 (same as Figure S12), the mean ozone
225 concentration of the downwind site (national monitoring station, NMS) was 27.6±21.8 ppb
226 day⁻¹ higher than the observation site (OS), slightly lower than the difference (~36 ppb day⁻¹)

227 between PIC-VOCs and observed VOCs, which indirectly supported the accuracy of our results.

228 We added the corresponding analysis in the revised manuscript in lines 324-334 “An upwind

229 O₃ and VOCs measurement combined with a trajectory analysis might provide an approach for

230 checking the accuracy of our results. Alternatively, conducting a transient O₃ production rate

231 analysis after subtracting the transport of O₃ with a regional model and/or satellite observation

232 might be another option. Unfortunately, neither the upwind measurement nor the regional

233 model simulation was available at the time of our study. To further check the accuracy of our

234 results, we chose August 4th as a test case to explore the influence of the transport of ozone on

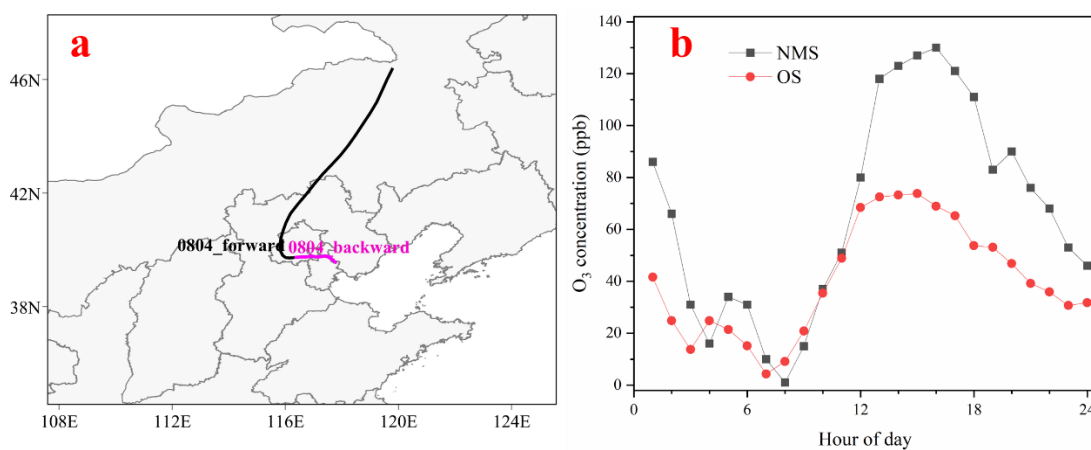
235 a downwind site based on the trajectory analysis. As shown in Figure S12, the mean ozone

236 concentration of the downwind site (national monitoring station, NMS) was 27.6±21.9 ppb

237 day⁻¹ higher than that of the observation site (OS), which was slightly less than the difference

238 (~36 ppb day⁻¹) between PIC-VOCs and observed VOCs and indirectly rationalized our

239 results.”.



240

241 **Figure R6.** The wind direction at the observation site on 4th Aug (a, backward and forward

242 meaning upwind and downwind, respectively) and the diurnal variation of ozone concentration

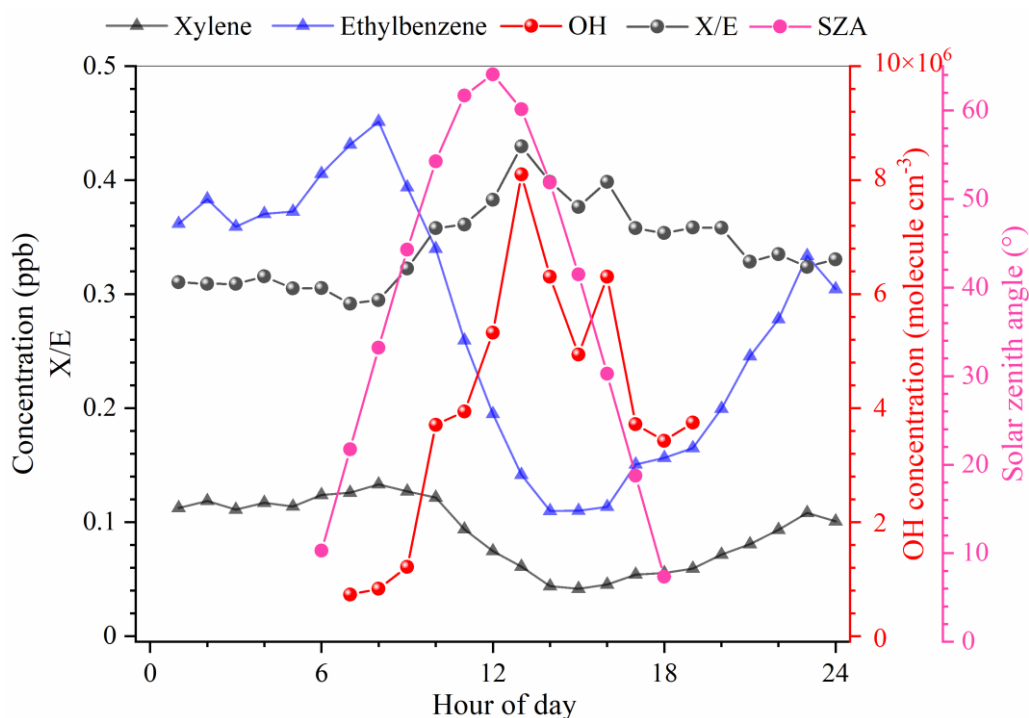
243 at observation site (OS) and one downwind site (national monitoring station (NMS)).

244

245 6. VOC correction: In Figure 1, the difference between the observed and “photochemical initial

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

256 **Response:** Thank you for your comments and good suggestion. The transition of the
257 initial VOCs should gradually increase with photolysis as you pointed out. Figure R7 (same as
258 FigureS7) shows the mean diurnal curves of the concentrations of xylene and ethylbenzene,
259 their ratio, the OH concentration and the solar zenith angle. The variation of solar zenith angle
260 was similar to that of J_{NO_2} (Figure R1). The OH concentration was from 0.82 to 8.1×10^6 ($4.3 \pm$
261 1.9×10^6), the ratio of xylene to ethylbenzene increased gradually (07:00~12:00). In the revised
262 manuscript in [lines 177-181](#), we added the sentences “**The ratio of xylene to ethylbenzene and**
263 **the OH exposure concentration are shown in Figure S7. The results showed that the ratio of**
264 **xylene to ethylbenzene increased gradually (07:00~12:00), which is consistent with the trend**
265 **of xylene and ethylbenzene. The OH exposure was from 0.82 to 8.1×10^6 molecule cm^{-3} h, with**
266 **a mean daytime value of $4.3 \pm 1.9 \times 10^6$ molecules cm^{-3} h.”.**



267

268 **Figure R7.** The mean diurnal curves of the concentration of xylene and ethylbenzene, their
 269 ratio, the OH exposure concentration (molecule cm⁻³), and solar zenith angle.

270 We double checked the PIC concentrations and the related dataset from 07:00 to 19:00 in

271 Figure 1. We are sorry for a stupid mistake when drawing Figure 1. We wrongly added the data

272 of 05:00 and 06:00 twice when calculating PICs of VOCs from 07:00 to 12:00, thus leading to

273 the sharp increase in the early morning (07:00-10:00). The simulation process using the PIC-

274 VOCs is correct. And we have corrected the Figure 1 (Figure R8) and the updated the sentences

275 in lines 259-265 in the revised manuscript “However, the photochemical initial concentrations

276 (PICs) of TVOCs, which varied from 2.2 to 27.8 ppb with a mean value of 24.5 ± 2.1 ppb,

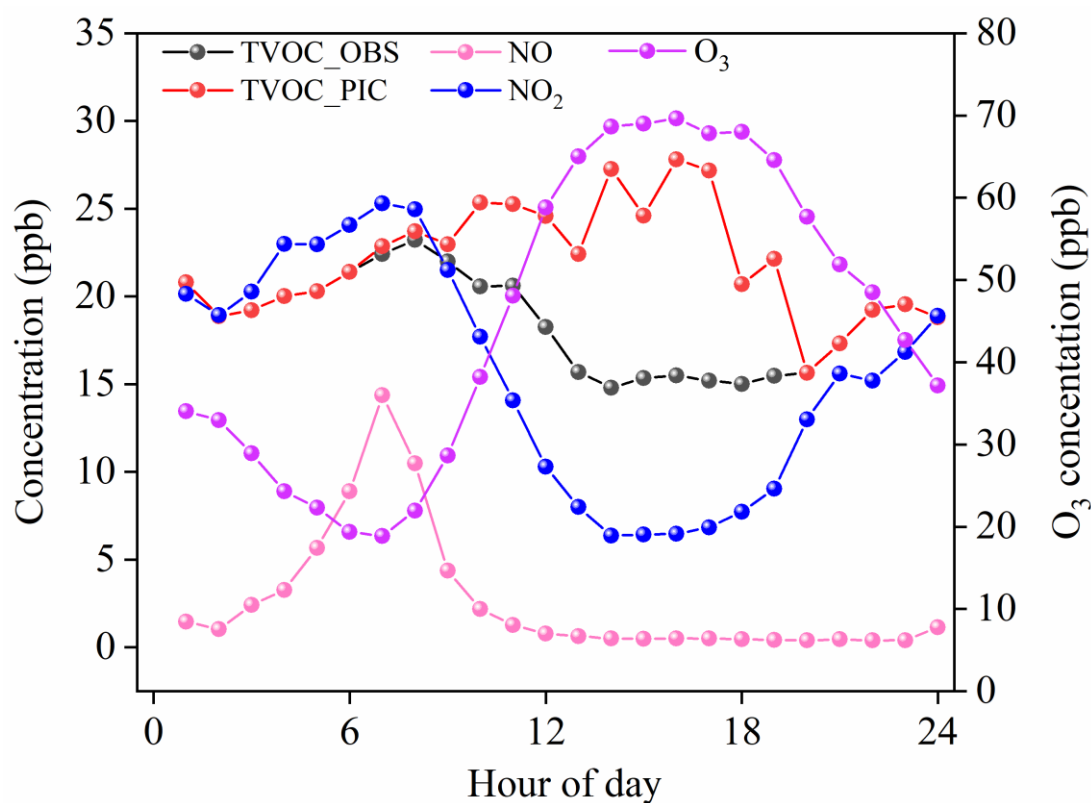
277 showed a different diurnal curve compared with the observed concentrations. It slightly

278 increased from 07:00 to 14:00, which was similar to the diurnal variation of VOCs in previous

279 work (Zhan et al., 2021). The average PIC-VOCs was 6.9 ± 0.5 ppb higher than the observed

280 concentration of TVOCs, indicating an underestimated contribution of the local

281 photochemistry of VOCs to O₃ and organic aerosol formation.”



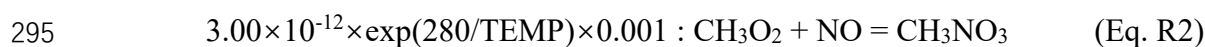
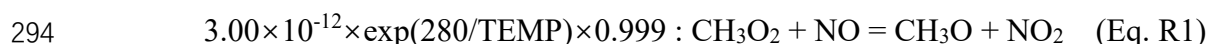
282

283 **Figure R8.** Overview of average diurnal variations of O₃, NO_x, and TVOC. **The data represent**
 284 **measured results, except for those of the TVOC_PIC, which are calculated based on OH radical**
 285 **exposure. The data range is August 1-28, 2019.**

286

287 7. Ozone production and loss metrics: Please discuss for Eq. 3 how alkyl nitrate formation is
 288 treated; is k_{RO_2+NO} the rate constants for only $RO_2 + NO$ reactions that produce RO and NO_2 ?
 289 If k_{RO_2+NO} is the rate for all $RO_2 + NO$ reactions, then the alkyl nitrate branching ratio must be
 290 accounted for.

291 **Response:** Thank you for your comments. We agree with you that the reaction between
 292 RO_2 and NO can produce both RO and alkyl nitrate. The branching ratio was actually accounted
 293 for in the model. For example,

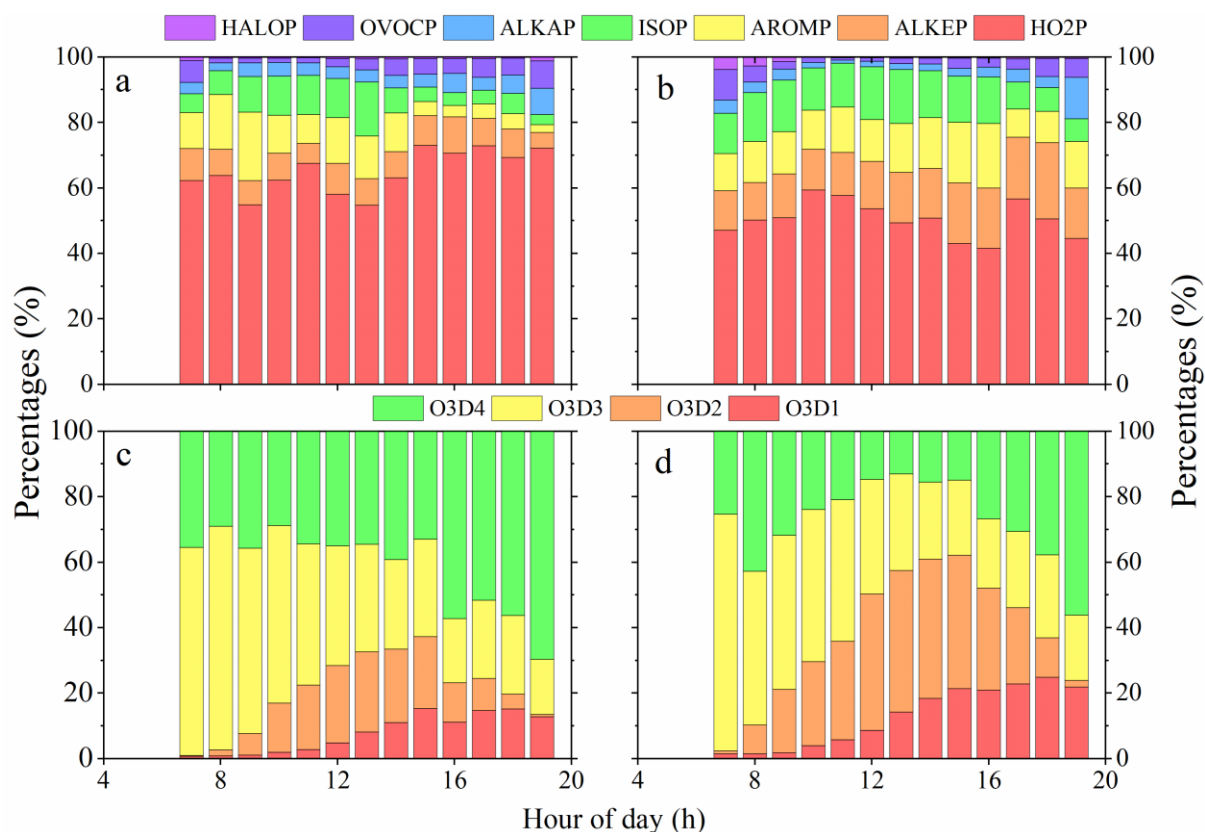


296 where, TEMP is the temperature, and the numbers of 0.999 and 0.001 are the branching ratio
 297 for Eq. R1 and R2, respectively.

298 When calculating the ozone production and loss in Eq.3, we just marked the RO path in
299 the master chemical mechanism, such as Eq. R1, and excluded the alkyl nitrate branch (Eq.
300 R2). Therefore, the k_{RO_2+NO} in Eq. 3 is indeed the reaction rate constant between RO_2 and NO
301 that produce the RO and NO_2 . In the revised manuscript, we clearly clarified it “ k_{HO_2+NO} is the
302 second reaction rate between HO_2 and NO ; and k_{RO_2+NO} is the second reaction rate for the
303 reaction between RO_2 and NO , which only produces RO and NO_2 .” in lines 214-215.

304
305 8. Relatedly, in Figure 3, a comparison of panels (c) and (d) appears to indicate that the loss of
306 ozone via reaction of O1D with H_2O increases when using PIC VOCs rather than measured.
307 Please elaborate why this is, is this just because there is more O_3 (and so more O1D) in the
308 model with PIC VOCs, and so the rate increases even through the amount of H_2O remains
309 constant? If so, it might help to include a companion figure to Figure 3 in the supplement that
310 shows $P(O_3)$ and $L(O_3)$ as percentages of O_3 production/loss to help the reader understand the
311 relative change in loss processes as well.

312 **Response:** Thank you for your comments and good suggestion. Yes, the loss rate of ozone
313 via reaction of O1D with H_2O ($2.2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298K, Atkinson et al., 2004) is
314 higher when using the PIC-VOCs than that between ozone and alkenes ($1.27 \times 10^{-17} \text{ cm}^3$
315 $\text{molecule}^{-1} \text{ s}^{-1}$ at 298K, Atkinson et al., 1994). Therefore, photolysis of ozone contributes more
316 O1D, leading to enhanced consumption of O_3 by H_2O . Figure R9 shows the percentages of
317 different paths of $P(O_3)$ and $L(O_3)$. The relative contributions of the reactions between O_3 and
318 alkenes (O1D3) and between NO_2 and OH (O1D4) to O_3 loss decrease calculated on the basis
319 of the PIC-VOCs when compared with the measured VOCs, while the it increases obviously
320 for other two paths, i.e. O3D1 and O3O2.



321
 322 **Figure R9.** The percentages of different ozone production and loss rate (observed VOCs in a
 323 and c, and PIC-VOCs in b and d). The upper and lower panels present the percentages of
 324 different ozone production and loss rate, respectively.

325
 326 We added the Figure R9 as Figure S13 in the SI. In the revised manuscript in [lines 345-](#)
 327 [349](#), we added a short paragraph “[Figure S13 shows the percentages of the different paths of](#)
 328 [P\(O₃\) and L\(O₃\). The relative contributions of the reactions between O₃ and alkenes \(O1D3\)](#)
 329 [and between NO₂ and OH \(O1D4\) to the O₃ sinks decreased when calculated based on PIC-](#)
 330 [VOCs compared with those of the measured VOCs, while they obviously increased for the](#)
 331 [other two paths, i.e., O3D1 and O3O2.”.](#)

332
 333 Minor comments

334 1. The argument made in lines 69-75 of the introduction about the different mixing ratios of
 335 VOCs at the source vs. measurement site is confusing on a first read because it is not clear that
 336 the scenario which applies here is where the source one is attempting to control with policy is
 337 significantly upwind of the measurement site. If we were considering a source (e.g. traffic)

338 which is closely clustered around the measurement site, then the VOCs measured at the site
339 will be the correct concentrations to consider for O₃ production.

340 **Response:** Thank you for good comments. We agree with you that the VOCs measured at
341 the site will be the correct concentrations to consider for O₃ production if we are considering a
342 source (e.g. traffic) which is closely clustered around the measurement site. However, on a
343 regional or urban scale, our argument is reasonable. In the revised manuscript, we have made
344 it clearer “The mixing ratios of VOCs observed at a sampling site are actually the residues of
345 VOCs from emissions due to the photochemical loss during transport from the source site to
346 the receptor site. If photochemically consumed VOCs are not considered, the O₃ formation
347 sensitivity and net O₃ production may be misunderstood, and subsequent policymaking on O₃
348 pollution prevention at regional or urban scales may be misguided. Thus, the photochemical
349 age-based approach has been applied to evaluate the effect of photochemical processes on VOC
350 measurements (Shao et al., 2011)” in lines 69-75.

351

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

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

358

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

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

364

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

368 **Response:** Thank you. In the revised manuscript, we have updated the caption of Figure
369 2 “The pentagons and stars indicate the status in the morning (09:00-10:00) and at noon
370 (14:00-15:00), respectively.” In lines 276-279 in the revised manuscript, we also updated the
371 specific time “The black full star and pentagon denote the observed concentrations of NO_x and
372 VOCs in the morning (09:00-10:00) and at noon (14:00-15:00), respectively, while the blue
373 symbols are the corresponding values of PICs”.

374

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

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

385 In lines 365-390 in the revised manuscript, we have updated this paragraph “The budget
386 of OH-HO₂-RO₂ radicals was further analyzed to understand the photochemical O₃ formation
387 process. The comparison of the radical budget derived from the observed and PIC-VOCs is
388 shown in Figure 4. The radical cycles are divided into radical sources (green boxes), radical
389 sinks (black boxes), radical propagations (red circles) and equilibria between radical and
390 reservoir species (yellow boxes). The numbers or percentages are the average formation rates
391 (ppb h⁻¹) or relative contributions of the corresponding reaction path based on the observed
392 VOCs (outside the brackets) and the PIC-VOCs (inside the brackets) to a certain radical. The
393 relative contributions of different radical paths based on the observed VOCs (outside the

394 brackets) were comparable with those reported in Beijing, Shanghai, and Guangzhou (Tan et
395 al., 2019), while variations were observed for some reaction paths based on the PIC-VOCs. For
396 example, the reaction between ozone and alkenes based on initial VOC concentrations
397 (percentages inside the brackets) contributed more to OH (from 7% to 21%) and HO₂ radical
398 production (from 6% to 12%), while photolysis of HONO and HCHO contributed less to the
399 production of OH (from 76% to 60%) and HO₂ radicals (from 44% to 40%), respectively. Other
400 radical sources were consistent between the two scenarios. Interestingly, the average formation
401 rates of OH, HO₂ and RO₂ radicals derived from the PIC-VOCs were obviously higher than
402 those from the observed VOCs. In particular, the oxidation of NO by RO₂ and HO₂ increased
403 by 1.6 and 1.3 ppb h⁻¹, respectively. The enhanced oxidation rate of NO was equal to the
404 increase in the average F(O₃) in the analysis process above. This meant that the radical
405 propagation of OH-RO₂-HO₂ sped up in the case of PIC-VOCs, subsequently accelerating the
406 chemical loop of NO-NO₂-O₃. For the radical sinks and equilibria related to HNO₄, RONO₂
407 and PAN, the values were basically comparable between the two scenarios. In addition, the O₃
408 formation from the RO₂ path increased by 4.1% (from 39.5% to 43.6%) in the simulation using
409 the PIC-VOCs compared with the observed VOCs. The above budget analysis explained the
410 observed increases in F(O₃) (~3 ppb h⁻¹), which were mainly driven by the reaction of missed
411 reactive VOCs, such as alkenes, with O₃.”.

412

413 Summary

414 While this paper is a fair study of how one might account for degradation of VOCs between
415 sources and measurements in order to formulate better approaches to controlling O₃ production,
416 there have been a number of earlier studies looking at this problem in Beijing. In my opinion,
417 in order for a revision to be considered for publication, the authors must revise the paper to

418 clarify what new information their work adds compared to the previous studies or refocus the
419 paper as a replication study or an update to more recent times. In this second case, the revision
420 should include a thorough comparison with previous studies of this effect in the Beijing area.

421 **Response:** Thank you for your comment. We have responded all your good comments
422 and suggestions aforementioned. In conclusion, we quantitatively discussed the influence of
423 VOCs degradation between sources and measurements on understanding ozone pollution based
424 on OBM simulations. When comparing with these previous studies estimating OFP with the
425 MIR method, this study has accounted for the non-linear relationship of O₃ formation to VOCs
426 and NO_x. In addition, we provide more details about this issue based on budget analysis of the
427 crucial radicals related to O₃ formation. An underestimation should be about 3 ppb h⁻¹ or 36
428 ppb day⁻¹ for O₃ production rate, which is mainly driven by the reaction between the missed
429 reactive VOCs, such as alkenes, with O₃ during our observation. In addition, highly reactive
430 alkenes by the photochemical oxidation accelerated the OH and HO₂ radical cycle.

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492

493 **Reviewer #2**

494 This manuscript uses a chemical box model approach to calculate VOC and NO_x loss rates,
495 radical chemistry and ozone production rates when constrained with pollutant concentrations
496 in a suburb of Beijing, China. Overall, I recommend revisions of the modelling approach.
497 Below are my specific comments.

498 **Response:** Thank you for your positive comments and good suggestions. We will respond
499 your comments point-by-point.

500

501 1. Line 43. Reference for Seinfeld is missing Pandis author.

502 **Response:** Thank you for your suggestion. We have updated the missing author in the
503 corresponding position. In addition, we have double checked and updated all references in the
504 revised manuscript.

505

506 2. Line 125. To compare the model vs measurements, it is advised to look at slope, intercept
507 and not just correlation coefficient.

508 **Response:** Thank you for your good suggestion. In the revised SI, we updated the Figure
509 S2 with adding the slope and intercept. We have also updated in the revised manuscript “The
510 correlation coefficient is 0.9 (with a slope of 0.7), indicating that the concentrations of NMHCs
511 are comparable using these two measurement techniques” in [lines 124-126](#).

512 It should be noted that in line 108, we are discussing the performance between the two
513 instruments for VOC measurements rather than that between the model and measurements.
514 When we comparing the performance of the model with measurements, the slope was also
515 added in addition to the correlation coefficient in the revised manuscript ([line 203](#)).

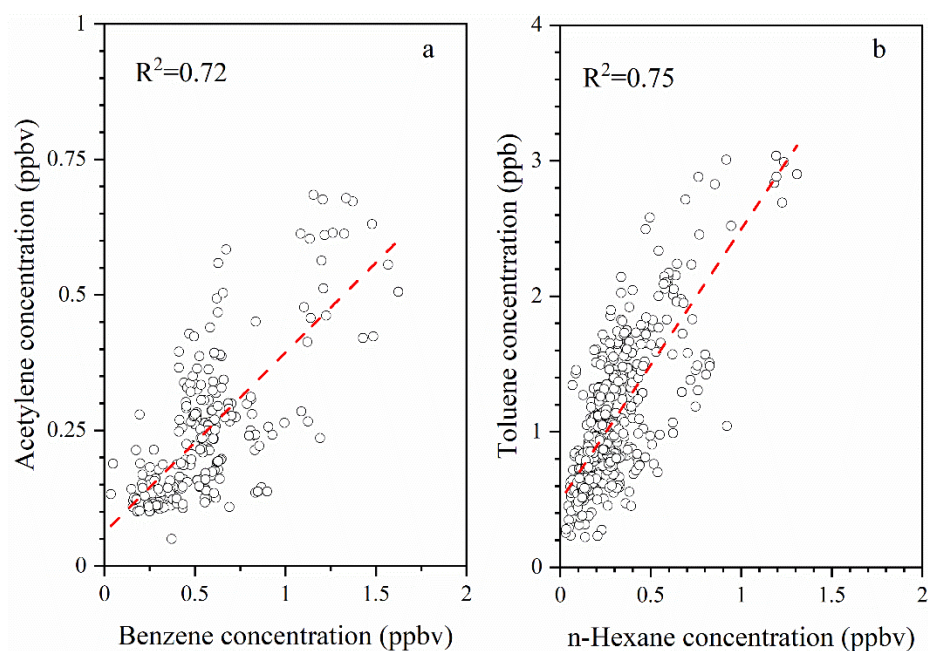
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518 3. Line 147. The hydrocarbon ratio photochemical clock concept works well when you have
519 an isolated source that co-emits the hydrocarbons and a receptor site with no emissions in
520 between. If there are different sources in between and also mixing of airmasses into the plume
521 with different photochemical ages then it complicates the concept and rationale. The use of an
522 early morning time to define the aromatic ratio is also not explained well. The early morning

523 measurements likely reflect the concentration of local emissions under a shallow inversion
524 layer. If the emissions are uniformly distributed across region, then this might be the best time
525 to estimate the emission ratio for xylene to ethylbenzene. The assumption that the emission
526 source remains constant over the region is questionable. It might be helpful to look at gridded
527 regional air quality emissions over the region and plot the emission ratio to see if it is relatively
528 uniform spatially.

529 **Response:** Thank you for good comments and suggestion. We agree with you that the
530 uniform distribution and constant emissions of VOCs sources are critical for calculating
531 chemical loss of VOCs using hydrocarbon ratio photochemical clock. At least, the emission
532 pattern of VOCs should be constant during the whole day when compared with that in the early
533 morning. Previous studies have found that the ambient ratios of VOCs can reflect their relative
534 emission rates from sources (Golden et al., 2000; Jobson et al., 2004). To verify the rationality
535 of this assumption, Shao et al (2011) had tested relative emission rates from sources by testing
536 different ambient ratios of four pairs of hydrocarbons, i.e., benzene vs acetylene, trans-2-butene
537 vs cis-2-butene, ethene vs toluene and n-hexane vs toluene, that having similar k_{OH} values in
538 each pair. We also further choose the benzene vs acetylene and n-hexane vs toluene to check
539 whether VOCs emissions are constant during our observations. The results are showed in
540 Figure R10 (same as Figure S5). The linear correlation coefficients (R^2) were higher than 0.7
541 and were equal to those reported by Shao et al (2011). This indicates that the assumption of a
542 constant VOCs emission should be reasonable during our observations.



543

544 **Figure R10.** The relationship between the concentration of toluene vs acetylene and n-

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hexane vs toluene.

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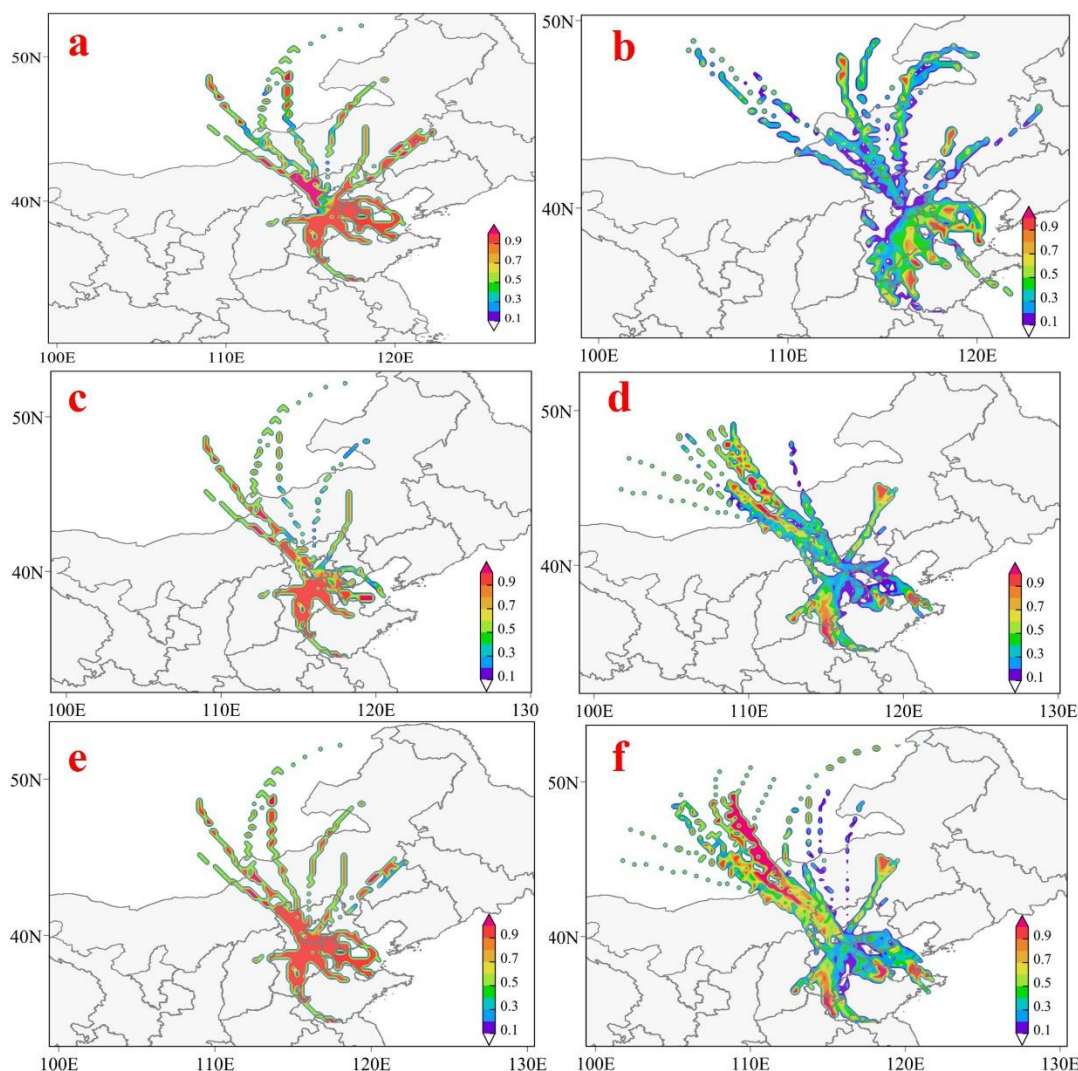
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As for the assumption that the emission source remains constant over the region, it is better to look at gridded regional air quality emissions over the region. Unfortunately, such regional gridded data are unavailable at the present time. Alternatively, we performed spatial distribution analysis using a source-receptor model (potential source contribution function, PSCF). In Figure R11 (same as Figure S6), the emissions of VOCs are not spatially uniform in Beijing, i.e., strong emissions are in the south or southeast directions. However, the PSCF patterns in the daytime are highly similar to that in the early morning. This means that the emissions of VOCs should be constant during the daytime.



554
 555 **Figure R11.** The potential source contribution function (PSCF) maps for the ratio of xylene to
 556 ethylbenzene (a and b), ethylbenzene (c and d), and xylene (e and f) arriving in the observation
 557 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
 558 are the results of daytime (07:00-19:00).

559
 560 In the revised manuscript, we added the sentences “. In previous work (Shao et al., 2011;
 561 Zhan et al., 2021), the selection of ethylbenzene and xylene as tracers was justified for
 562 calculating ambient OH exposure under the following conditions: 1) the concentrations of
 563 xylene and ethylbenzene were well correlated (Figure S4), which indicated that they were
 564 simultaneously emitted; 2) they had different degradation rates in the atmosphere; and 3) the
 565 calculated PICs were in good agreement with those calculated using other tracers, such as i-
 566 butene/propene (Zhan et al., 2021). To test the relative constant emission ratio from different

577 sources, we chose benzene vs. acetylene and n-hexane vs. toluene as references, and the result
578 is shown in Figure S5. These ambient ratios could directly reflect their relative emission rates
579 from sources (Goldan et al., 2000; Jobson et al., 2004). The linear correlation coefficients (R^2)
580 were generally higher than 0.7, which were equal to that reported by Shao et al. (2011). To
581 further test the assumption that the emissions of xylene and ethylbenzene were constant
582 throughout the day, their potential sources were calculated using a source-receptor model (the
583 potential source contribution function, PSCF). As shown in Figure S6, xylene and ethylbenzene
584 showed similar distributions. In addition, the ratio of ethylbenzene/xylene at 5:00 and 6:00 was
585 similar to that during the daytime. These results indicated that the emissions of xylene and
586 ethylbenzene were constant throughout the day.” in lines 160-175. In future, we will try to
587 combine OBM and the regional air quality model to better understand the influence of
588 photochemical initial VOCs.

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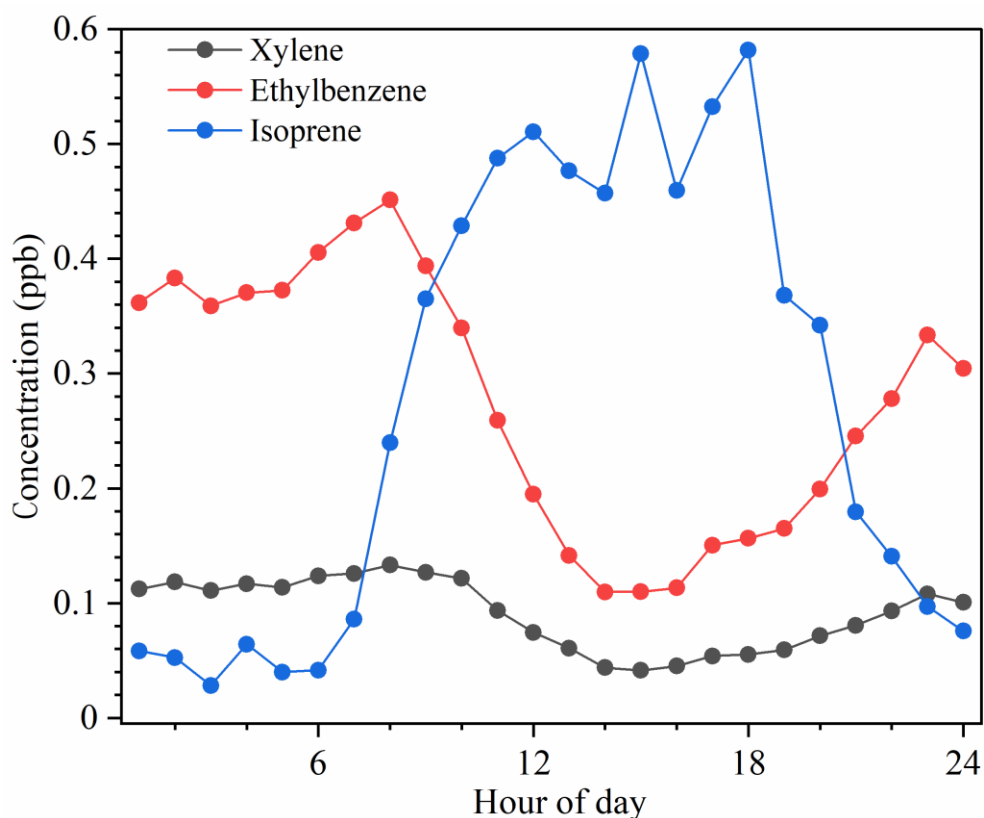
580 4. Line 178-182. The mean daytime OH used for the calculation was $4.3E6$ molec/cm³. Please
581 state that the measured aromatic ratio was also a mean value for the same daytime period used
582 to calculate the OH.

583 **Response:** Thank you for good comments. Indeed, here we are discussing the daytime
584 OH exposure (molecules cm⁻³ h) but not OH concentration (molecules cm⁻³). We calculated
585 hourly OH exposure from 07:00 to 19:00 using the ratio of xylene to ethylbenzene according
586 to Eqs.1 and 2 in the manuscript. Then, we obtained the mean daytime OH exposure 4.3 ± 1.9
587 molecules cm⁻³ h. The mean daytime OH concentration ($4.3\pm 1.9\times 10^6$ molecules cm⁻³) was
588 calculated based on the JO1D using the method reported in our previous work (Liu et al., 2020b,
589 Liu et al., 2020c). In lines 178-182 in the revised manuscript, we rephrased the sentences to
590 make it clearer “The OH exposure was from 0.82 to 8.1×10^6 molecule cm⁻³ h, with a mean
591 daytime value of $4.3\pm 1.9\times 10^6$ molecules cm⁻³ h. Accordingly, the mean photochemical ages
592 were 1.7 ± 0.9 h using the mean daytime (8:00-17:00 LT) OH concentrations ($4.3\pm 3.1\times 10^6$
593 molecules cm⁻³) calculated based on JO1D using the method reported in our previous work
594 (Liu et al., 2020b; Liu et al., 2020c).”.

595

596 5. Line 185. I agree that the biogenic isoprene emission is not co-located with the aromatic
597 emission sources and this complicates the ratio method. Can the authors look at regional model
598 emissions for isoprene to see if the isoprene sources are local near the site or whether they are
599 closer to the aromatic sources? A possible assumption is that the production and loss of isoprene
600 balance along the transport and concentration of isoprene remain constant in the trajectory from
601 the aromatic source region to the site. Again, regional air quality model results would be able
602 to show what the distribution of isoprene looks like around the site.

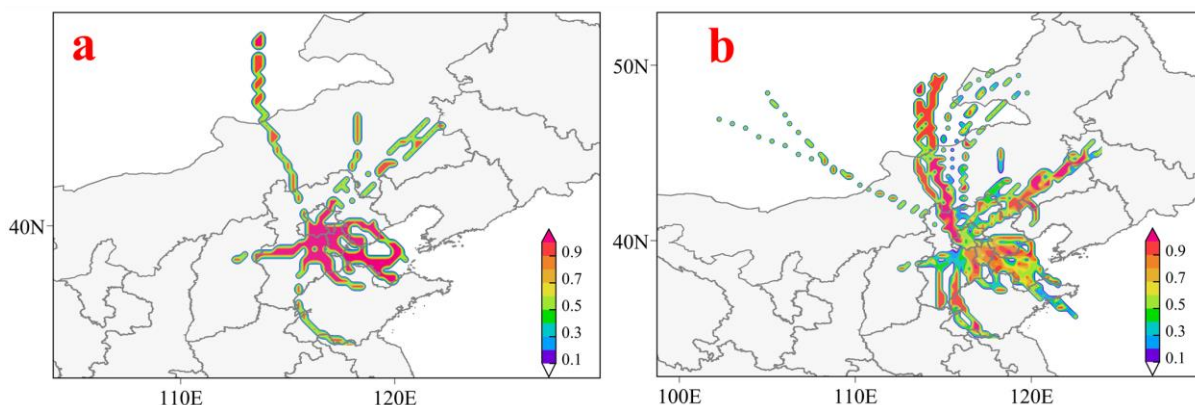
603 **Response:** Thank you for good suggestion. We think that isoprene is mainly from biogenic
604 emissions in summer but not co-located with the aromatic emission sources. This is evidenced
605 by the diurnal variations of isoprene, xylene and ethylbenzene (Figure R12, same as Figure
606 S14) although the regional model emissions for isoprene are unavailable at the present time.
607 As shown in Figure R12, isoprene and aromatics (xylene and ethylbenzene) showed totally
608 different diurnal variations. This means isoprene sources are from biogenic emissions.



609
610 **Figure R12.** The mean diurnal curves of xylene, ethylbenzene and isoprene.

611 On the other hand, like xylene and ethylbenzene, we also carried out PSCF analysis
612 (Figure R13, same as Figure S15) for isoprene to check whether the production and loss of

613 isoprene is balanced along the transport and concentration of isoprene remain constant in the
614 trajectory from the aromatic source region to the site. The results showed that the spatial pattern
615 of isoprene is even during our observations. This indirectly indicated that it could be considered
616 as the balance on production and loss of isoprene along the transport, and the concentration of
617 isoprene remain constant in the trajectory from the aromatic source region to the site.



618
619 **Figure R13.** The potential source contribution function (PSCF) maps for the isoprene arriving
620 in the observation site. The figures of a and b are the results of 05:00 and 06:00, and the daytime
621 (07:00-19:00), respectively.

622
623 In lines 124-130 in the revised SI, we added the sentences “Isoprene is mainly from
624 biogenic emissions but not co-located with the aromatic emission sources in summer, which is
625 evidenced by the diurnal variations of isoprene, xylene and ethylbenzene (Figure S14) although
626 the regional model emissions for isoprene are unavailable at the present time. The results of
627 PSCF analysis showed that the spatial pattern of isoprene is even during our observations in
628 S15, which indirectly indicated that it could be considered as the balance on production and
629 loss of isoprene along the transport, and the concentration of isoprene remain constant in the
630 trajectory from the aromatic source region to the site.”.

631
632 6. Line 233. I would recommend “grouped into lumped species” instead of parcels.

633 **Response:** Thank you for good suggestion. We have updated “the observed VOCs are
634 grouped into different lumped species according to the classification of RACM2” in the lines
635 233-235 in the revised manuscript.

636

637 7. Line 238. Five minutes is enough time for the radicals to reach steady-state but not the NO_x
638 and OVOCs. For example, PAN has a long lifetime and would not reach steady state in 5 min.
639 Given that the intent is to “correct” the VOCs to an initial condition and you expect an ~ 2hr
640 photochemical time then an equivalent time to run the model might be best approach and would
641 give time for OVOCs to spin up to more reasonable mixing ratios.

642 **Response:** Thank you for comments and suggestion. The time interval for the outputs is
643 usually set to 60 min (Lu et al., 2013; Lu et al., 2017; Tan et al., 2019) determined by the time
644 resolution of observation data. However, the time interval of 60 min is too coarse to run the
645 model because the sun can move a lot within one hour. Therefore, a higher time resolution (5
646 min) is usually taken along with interpolation of the inputs in OBM simulations to reduce the
647 influence of great distortion of meteorological parameters in a long-time interval (Tan et al.,
648 2017). The time interval (60 min) in this study is similar with that used by Lu et al (2013) and
649 Lu et al (2017), and higher than that (30 min) reported by Tan et al (2018), which indicated that
650 the photochemical time setting was acceptable. We agree with you that OVOCs and PAN have
651 a long lifetime compared with the radicals (OH, HO₂ and RO₂). Although the long lifetime
652 species would not reach steady state in 5 min, the model outputted their concentrations with a
653 time resolution of 60 min. This indeed accounted for the time for OVOCs and PAN to spin up
654 to more reasonable mixing ratios. In addition, the chemical cycle of radicals is critical for ozone
655 formation. The simulation is more reliable once the radical sources, sinks and propagation of
656 radicals can be well simulated at this time interval.

657 In the revised manuscript, we have updated the sentences “**The chemical model simulated**
658 **photochemical reactions with input species for a time interval of 60 minutes, which was enough**
659 **for NO_x, OH, HO₂, and RO₂ to reach a steady state because the typical relaxation time of the**
660 **chemical system is 5-10 minutes in summer (Tan et al., 2018). However, all the species and**
661 **parameters were input at a 5 min interval by data interpolation to reduce simulation**
662 **inconsistencies and large distortions of meteorological parameters at longer time intervals (Tan**
663 **et al., 2018)” in lines 235-240.**

664

665 8. One major concern that I have in the photochemical initiation of VOCs is that the authors

666 are not considering the correction needed for NO_x as it also reacts in the trajectory reaching
667 the site. The VOCs and NO_x can be emitted by common combustion processes, particularly in
668 an urban area. The authors also note they follow the same diurnal profile as VOCs. The lifetime
669 of NO_x is comparable to some VOCs so why not correct the NO_x as well? Other studies have
670 done this and in fact the NO_x/NO_y is an alternative ratio in the photochemical clock method
671 (Hayes et al., 2013).

672 **Response:** Thank you for good comments and suggestion. We agree with you that
673 photochemical conversion of NO_x should be corrected. Because the NO_y concentrations were
674 unavailable during our observations, we simply corrected the concentration of NO and NO₂
675 using the OH exposure and assuming a gas phase oxidation by OH radical ($k_{\text{NO-OH}}=3.0\times 10^{-11}$
676 $\text{cm}^{-3} \text{ molecules s}^{-1}$ and $k_{\text{NO}_2\text{-OH}}=1.2\times 10^{-11} \text{ cm}^{-3} \text{ molecules s}^{-1}$, Atkinson et al., 2004). The
677 corrected data are showed in Figure R14. The average concentrations of NO, NO₂, and NO_x
678 were underestimated 0.6 ± 0.6 ppb, 1.5 ± 1.4 ppb, and 2.1 ± 2.0 ppb, respectively, lower than the
679 underestimated VOCs (6.9 ± 0.5 , Figure 1), which indicated that the role of the photochemical
680 loss of NO_x is less important than VOCs when evaluating the ozone formation process and
681 mechanism. In the early morning, the PICs of NO_x were almost the same as the observed values.
682 On the other hand, the previous studies (Li et al., 2020; Tan et al., 2019; Sun et al., 2011) have
683 showed that the Beijing belonged to VOCs-limited regime, which means that the NO_x is
684 sufficient during the nonlinear relationship of NO_x-VOCs-O₃. In other word, the chemical loss
685 of NO_x compared with photochemical loss of VOCs was less important in Beijing. Therefore,
686 we focus on the contribution of photochemical loss of VOCs to ozone formation mechanism
687 in this study. And in future, we will compare the ratio of NO_x to NO_y (alternative calculation)
688 with the ratio method of xylene to ethylbenzene.

706 maximal mean ozone concentrations during our observations (Figure 1). When we diagnosing
707 the chemistry pathways (Figure 3 and 4), we have constrained O₃ concentrations. Thus, this
708 ensures the ozone is at a reasonable level for calculating the reaction rates between alkene and
709 ozonolysis, and between O₁D and H₂O.

710 In the revised manuscript, we have added a sentence “It is worth mentioning that the
711 average survey data were selected as the baseline scenario in simulating the EKMA curve in
712 this study.” in lines 241-242.

713

714 10. Line 313. The daytime average P(O₃) is calculated at 3 ppbv/hr higher than with using
715 measured VOCs. The authors appear to extrapolate to a 24-hr average by multiplying by 24 hr
716 to get 36 ppbv/hr higher than with the measured VOCs. The nighttime P(O₃) averages could be
717 different than daytime averages, so it would be preferred to state what the daytime average
718 difference is between corrected and measured VOC approaches.

719 **Response:** Thanks for your good comments. The OBM in this study was just used to
720 simulated the daytime photochemical process (07:00~19:00 LT). Thus, the daytime average of
721 F(O₃) is 3.0±2.1 ppb h⁻¹ higher than with using measured VOCs. And the value of ~36 ppb day⁻¹
722 ¹ is just calculated from 07:00 to 19:00 based on the average F(O₃), not including the nighttime.

723 In the revised manuscript, we updated the sentences “The average daytime P(O₃) from
724 07:00 to 19:00 based on the initial concentrations of VOCs was 4.0±3.1 ppb h⁻¹ higher than
725 that based on the measured VOCs concentrations (Figure 3b). At the same time, the F(O₃) from
726 07:00 to 19:00 based on the initial concentrations of VOCs was also 3.0±2.1 ppb h⁻¹ higher
727 than the measured counterpart (Figure S11). Thus, the net O₃ production could be
728 accumulatively underestimated by ~36 ppb day⁻¹ from 07:00 to 19:00 if the consumption of
729 VOCs was not considered.” in lines 310-315.

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731 11. Line 432. I think the discussion of the diurnal profile and the different chemical and
732 transport processes should include the mixing of the stable nocturnal surface layer in the mid-
733 morning. As the sun heats the surface, there is significant mixing of surface layer with air above
734 in the residual atmospheric layer which is likely composed air from the prior day mixed
735 boundary layer and then transported to the site overnight. This residual air likely contains

736 hydrocarbons and ozone from different sources and at different photochemical ages. The ozone
737 increase around 9-10am is often associated with this vertical mixing. The ozone mixing down
738 to surface is photochemically produced but from a different region from previous days (unless
739 the region is influenced by a lake/land breeze where recirculation of the same air mass can
740 occur.

741 **Response:** Thanks for your good comments. We agree with you that the diurnal profile of
742 ozone will be affected by the mixing of the stable nocturnal surface layer in the mid-morning.
743 It should mention that $R(O_3)$ is the physical transportation including horizontal and vertical
744 mixing, and we attributed the variation of ozone in the morning all to the transportation. In fact,
745 the upper layer is known as the residual layer (RL) in the morning, which is isolated from the
746 surface due to inversion at night (Tan et al., 2021). RL usually contains the air mass with higher
747 O_3 concentration than that of nocturnal boundary layer, and when the boundary layer is
748 gradually uplifted, the vertical transport was important due to the fast entrainment.

749 In the revised manuscript, we have added the sentences “**This was mainly because the**
750 **residual layer (RL) that formed at night was unfavourable for the inversion of airmass in the**
751 **early morning (Tan et al., 2021). The RL usually contains an airmass with a higher**
752 **concentration of O_3 than that in the nocturnal boundary layer. Vertical transport becomes**
753 **prominent due to the fast entrainment when the boundary layer is gradually uplifted.”** in [lines](#)
754 [433-437](#).

755
756 12. Line 388. The authors state that “The radical budget analysis illustrated that the O_3
757 formation processes between the observed and photochemical initial VOCs showed no
758 significant difference.” The title of the manuscript implies that the initial photochemical loss
759 of VOCs does have an impact on the ozone formation mechanism. It seems that the ozone
760 production rates are sensitive to the corrected VOC loss (and likely corrected NO_x loss as well).
761 Maybe an improved title could be “Influence of Photochemical Loss of VOCs and NO_x on
762 Ozone Formation Rates and Diagnosed Ozone Production Sensitivity in Beijing, China”

763 **Response:** Thank you for comments and suggestion. As above, the chemical loss of NO_x
764 compared with photochemical loss of VOCs was less important in Beijing, and we focus on
765 the contribution of photochemical loss of VOCs to ozone formation mechanism in this study.

766 Actually, the current title “Influence of Photochemical Loss of VOCs on Understanding Ozone
767 Formation Mechanism” might also reflect what you mean. However, we still prefer the original
768 one to make it more concise.

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770 13. Figure S9 shows some days with large model over-predictions. Can the authors explain
771 what factors are contributing to the model over-predictions?

772 **Response:** Thank you for good comments. The OBM is zero-dimensional atmospheric
773 modeling coupled with just gas-phase reaction, which means that it cannot consider the
774 influence of meteorological process (vertical diffusion and horizontal transportation). The
775 dilution caused by wind or boundary layer was not well represented during the simulation, and
776 this may lead overestimation or underestimation to some extent. The similar over-predictions
777 were also reported by Zong et al (2018) and Zhang et al (2020), but it cannot affect the
778 simulation of ozone formation process and mechanism because we have the constrained ozone
779 concentration during simulations. In the revised manuscript, we added the sentences “It is
780 worth mentioning that the results of model simulation can sometimes be overestimated or
781 underestimated to some extent, which has also been reported by previous studies (Zong et al.,
782 2018; Zhang et al., 2020), but this did not affect our simulations of the ozone formation process
783 and mechanisms because we constrained the ozone concentration during our simulations.” in
784 [lines 204-208](#).

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786 14. Overall, I really like Figures 3, 4 and 5. My recommendation would be to include a NO_x
787 correction, as well as the VOC correction, and to consider a longer model time so that the
788 OVOCs reach closer to their typical ambient concentrations. Of particular interest would be
789 the aromatic and monoterpene oxidation products as the precursor aromatic and monoterpene
790 have an intermediate lifetime (several hours) and their OVOCs are not typically measured.

791 The figures are of very good quality. The paper needs some improvements for English language.

792 **Response:** Thank you for your positive comments and good suggestions. We have
793 carefully responded to all of your point-by-point comments and issues above and have revised
794 the manuscript and SI accordingly. We also carefully corrected language errors by a native
795 speaker (as shown in Figure R6). The corrections have been marked in blue in the revised
796 manuscript.



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798 **Figure R6.** The editing certificate by the highly native English speaking editors at AJE.

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