The authors present a comprehensive analysis from the perspective in both observations and model simulation to uncover the reason for the high-level Ozone concentration during Shanghai's static management. And by comparing the similar experiments conducted during the same period in 2020 and 2021, they find that the average concentration of ozone was nearly 23% higher during the static management compared to 2020 and 2021, despite the concentrations of VOCs and NOx decreased approximately 30% and 50%. With cluster analysis of diurnal patterns of ozone concentration, they conclude that the increasing days with high ozone levels leads to an overall high average concentration of ozone during the static management. And with a model to simulate the chemical process, they find that the higher VOCs/NO_2 ratio during the static management strengthens the radical cycle and which leads to an active photochemical process.

First, thank you for reviewing my manuscript. We found some issues with the photolysis data and have rerun the OBM model. We've also rechecked the results in Section 3.3. The new findings don't change the original conclusions much. My replies to your comments are based on these new results.

There are the comments to improve the manuscript: Reference:

Some of the references are missed in the main context, for example:

(1) line 33-35, (2) line 158-159, (3) line 231-234

R: Thanks for your correction. We have inserted relevant reference information, please refer to Line 34, Line 167, and Line 252.

Typo, format and description:

(1) line 52: during (should be During)

R: Thanks for your correction. We have modified it, please refer to Line 59.

(2) may be simply the units for the whole manuscript, for example, in line 129: "36.8±24.1 ug m^{-3}, 30.0±23.1 ug m^{-3}, and 21.8±14.0 ug m^{-3}" can be written as "36.8±24.1, 30.0±23.1, and 21.8±14.0 ug m^{-3}", and this information is related to Figure 1d, it should be noticed.

R: Thanks for your correction. We have modified it, please refer to Line 136.

(3) some of the arrows in Figure 4d were submerged and not able to see

R: Thanks for your correction. To be more reader-friendly, we've enlarged the arrows and changed their colors, as shown in Figure R1.

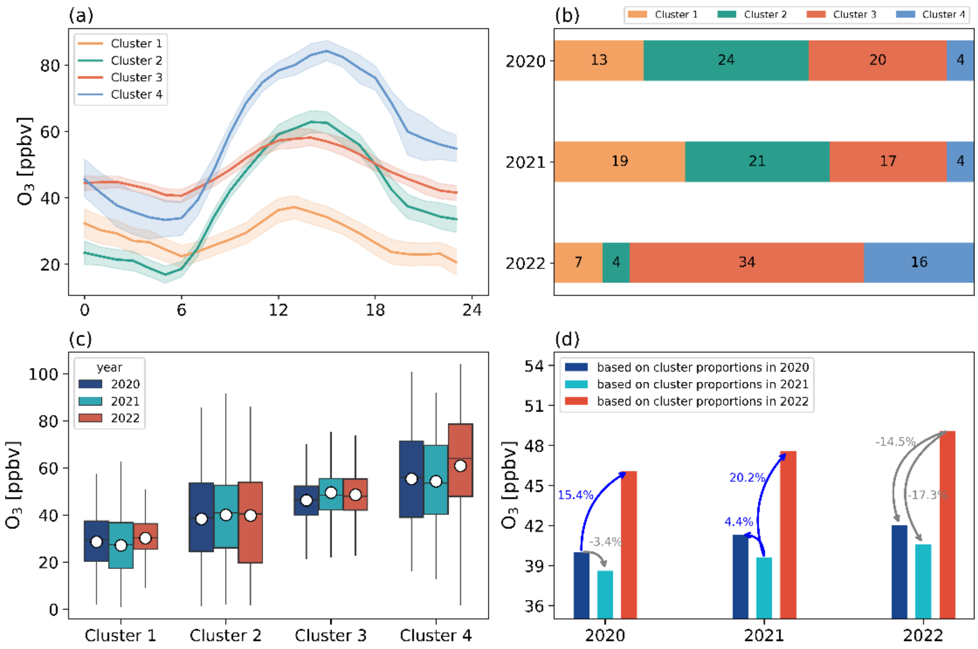

Figure R1. (a) Comparison of the mean diurnal profiles of the four types of O_3 after clustering. Colored areas denote 95% confidence intervals; (b) The proportions of the four clusters in 2020, 2021 and 2022. (c) Comparison of the O_3 levels of the four clusters in 2020, 2021 and 2022. The top and bottom of the vertical line for each box correspond to the 95th and 5th percentiles, respectively. The dots represent the averages, and the top, middle, and bottom lines of the box mark the 75th, 50th, and 25th percentiles, respectively; (d) Comparison of the average ozone concentrations in 2020, 2021 and 2022 for different ratios of the four clusters.

(4) the content in line 201-203 is corresponding to Figure 5, it should be noticed

R: Thanks for your correction. We have modified it, please refer to Line 217.

(5) nothing was written for the $PM_{2.5}$ profiles in Figure 5d

R: Thank you for your reminder. The daily variations of $PM_{2.5}$ under four clusters exhibit similar patterns to those of VOCs. We have added the "*The diurnal profiles of PM2.5 under four clusters exhibit similar patterns to those of VOCs, with Cluster 2 and Cluster 4 exhibiting a distinct morning peak.*" to the manuscript. Please refer to Lines 225-226.

(6) line 219: the unit of OH was missed, and the corresponding years should be specified

R: Thanks for your correction. We have modified it, please refer to Line 237.

(7) line 247: the (average) rate of

R: Thanks for your correction. We have modified it, please refer to Line 268.

(8) line 248: "which has an average rate of around 0.02 ppbv h-1", does this average rate is for the three years? It should be noticed.

R: Thanks for your comment. Yes, this average rate is for the three years. We have noticed it, please refer to Line 270.

(9) line 254: RO_2 (should be RO_2)

R: Thanks for your correction. We have modified it, please refer to Line 275.

(10) line 274: cm^3 (should be cm^{-3})

R: Thanks for your correction. We have modified it, please refer to Line 295.

(11) line space and post paragraph space for the title of Figure 7.

R: Thanks for your correction. We have modified it, please refer to Line 316.

(12) line 313: interfered (should be inferred)

R: Thanks for your correction. We have modified it, please refer to Line 342.

(13) line 323: that , there (should be that, there)

R: Thanks for your correction. We have modified it, please refer to Line 352.

(14) line 328: The average (ozone) concentration

R: Thanks for your correction. We have modified it, please refer to Line 357.

Comments:

(1) For the title: "Why Did Ozone Concentrations Increase During Shanghai's Static Management?" does it precise to say increase? As the fact is that the O_3 concentration keeps in high level during the static period, instead of an increasement.

R: Thanks for your comment. We agree with your statement, it is a rigorous statement. We have changed the title to "Why Did Ozone Concentrations Remain High During Shanghai's Static Management? A Statistical and Radical Chemistry Perspective".

(2) In line 136-138: "The literatures have shown that Shanghai in the spring largely operates under VOCs-limited regime (Li et 137 al., 2021a; Xue et al., 2022). Therefore, the reduction in VOCs during the static management period may not be enough to counteract the titration effect of NOx, and may even alter the ozone formation regime in Shanghai." What is the final conclusion for this prediction based on the current work, does the ozone formation regime changed in the static period?

R: Thanks for your comment. Based on the existing analysis, the free radical chemistry simulation results indicate that such a proportional decrease in precursors in Shanghai would enhance the radical cycling without altering the ozone formation regime.

(3) In line 179-181, four type clusters were described according to the background concentration and net production of ozone, can the authors provide more information on how these two parameters were obtained?

R: Thanks for your comment. We define the minimum concentration in the ozone diurnal profile as the background concentration, and the difference between the midday peak and the morning trough represents the net ozone production. By examining the ozone diurnal profiles of the four clusters, we can determine these two parameters. In this study, the background concentration and net generation of Cluster 1 are approximately 23 ppbv and 15 ppbv, respectively; for Cluster 2, they are 17 ppbv and 46 ppbv; for Cluster 3, 41 ppbv and 17 ppbv; and for Cluster 4, 33 ppbv and 51 ppbv, respectively.

We have included the information about these two parameters in the manuscript, please refer to Line 190-196.

(4) In line 192-193, it says: "Purely statistical analysis indicated that the significant increase in ozone levels in 2022 was due to a higher proportion of Cluster 3 and Cluster 4, which had higher ozone concentrations during the static management period.", Maybe it is not good to say "significant increase in ozone level", maybe "significant high and stable level of ozone" better?

R: Thank you for your constructive feedback. We appreciate your suggestions and have made the necessary revisions. Please refer to Line 206-207.

(5) In line 165-166, it says: "Consequently, the rise in OVOC proportion during the static management period has the potential to enhance the photochemical process". However, when the simulation results presented in line 237-267, the influence of the proportion change of OVOCs in 2022 on O_3 was not mentioned, can the conclusion be draw according to the model results?

R: Thanks for your comment. VOCs are both a source of radicals and a consumable in the propagation of radicals. The effect of changes in the concentrations and ratios of the VOCs components on the photochemical processes was analyzed from the point of view of the sources and sinks of the radicals. Figure R2 shows the proportion and daily variation of primary sources of radicals. We can see that in 2020, 2021 and 2023, the primary sources involved in the photolysis process were the main ones, accounting for 81.7%. 71.9% and 83.5%, and reactions with VOCs (mainly alkenes) accounted for 18.3%, 28.1% and 26.5% respectively. The results show that although the decrease in VOCs concentration in 2022 has led to a decrease in the intensity of reactions with VOCs as primary sources of radicals, the proportion of reactions with VOCs was close to the level in 2021. This shows that the reaction with VOCs to generate radicals was still important during the static management period. In addition, the proportions of OVOCs photolysis in 2020, 2021 and 2022 were 14.3%, 19.6% and 10.6% respectively. The photolysis of OVOCs in 2022 was lower in level and proportion than in 2020 and 2021, so from the perspective of radical sources, there is no direct evidence that the change in the concentration proportion of OVOCs during static management would enhance the photochemical process.

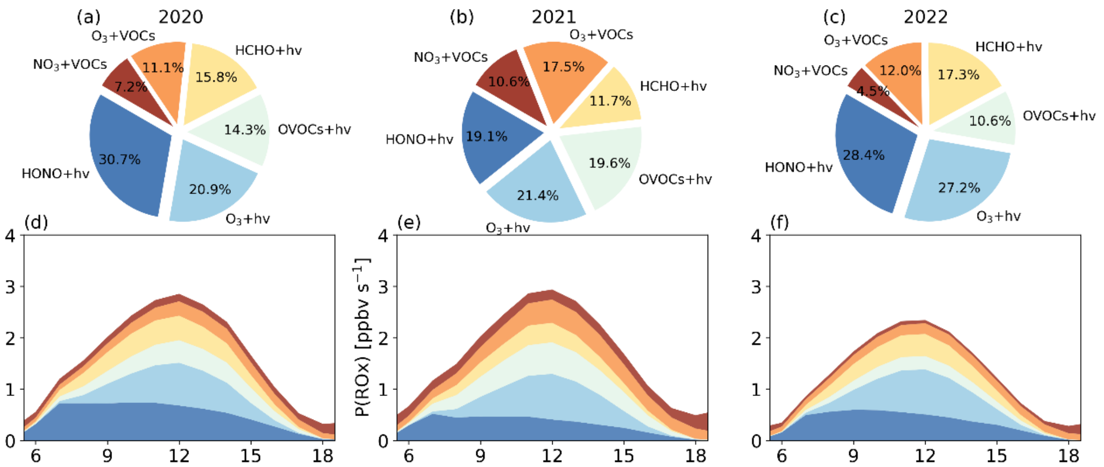

Figure R2. The proportions (a, b, c) and the mean diurnal profiles (d, e, f) of primary sources of daytime radicals during the periods from April to May of 2020, 2021, and 2022.

The radical cycle begins with the degradation of VOCs triggered by OH radicals. A widely used indicator of atmospheric oxidative capacity is the OH reactivity (*k*OH), defined as the reaction rate coefficient multiplied by the concentration of OH reactants, depending on the abundance and composition of major pollutants. Figure R3 illustrates the proportions of OH reactivity contributed by different VOCs components and its daily variation. In 2020, 2021 and 2022, the total *k*OH contributed by VOCs was 2.1 s^{-1}, 2.6 s^{-1} and 1.1 s^{-1}, respectively. Due to the influence of static management, the different proportions of decline of different components led to changes in the contribution to *k*OH. The contribution of aromatics decreased from 27% in 2020 and 31.6% in 2021 to 12% in 2022, while the contribution of olefins increased from 40.8% in 2020 and 43.3% in 2021 to 54.2% in 2022. And the contribution of OVOC did not change significantly. Alkenes play a large role from a radical propagation perspective, but there is no direct evidence that changes in OVOC concentration proportions would enhance photochemical processes.

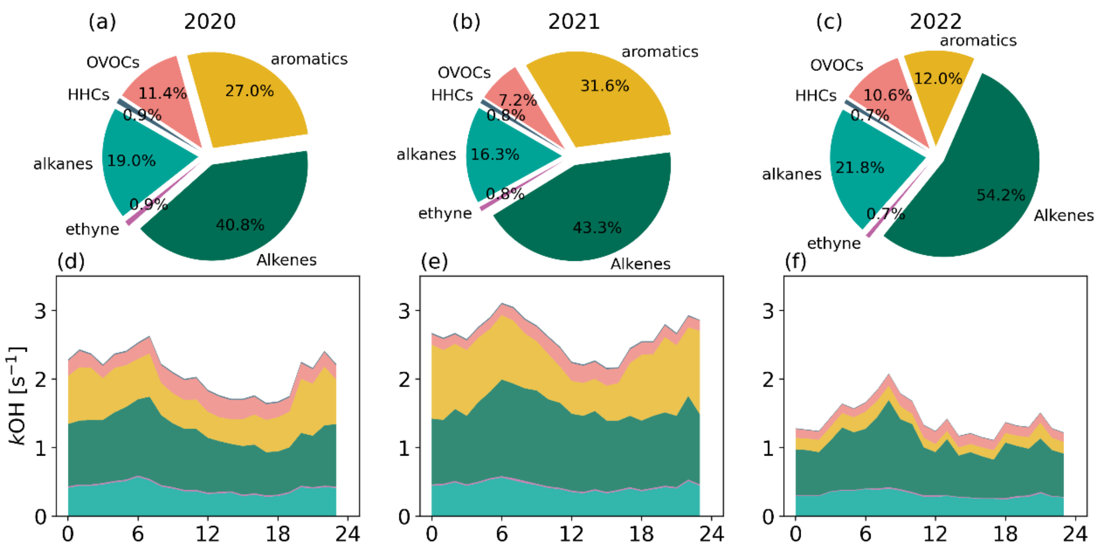

Figure R3. The proportions (a, b, c) and the mean diurnal profiles (d, e, f) of kOH for different VOCs components during the periods from April to May of 2020, 2021, and 2022.

Therefore, it is rather arbitrary to judge in the manuscript that an increase in the proportion of OVOC concentration is likely to enhance photochemical processes just from the change in concentration. Thanks for your comments, we have revised our hypothesis about the role of OVOCs in the manuscript. Please refer to Line 174-176.

"*In the radical chemistry section, the photolysis of OVOCs, as well as the reactions of O_3 and NO_3 with VOCs, have been quantified for their contributions to the radicals. Additionally, the role of VOCs in the propagation of radicals has been quantified.*".

(6) The information in line 256-257 is for the total P(ROx), but it was not shown in the Figure 6, maybe it should be added to directly see? The same for line 279-280, the total daily P(ROx) was not shown in Figure d-e for different clusters.

R: Thanks for your comment. Following your suggestion, Thank you for your comments. In accordance with your suggestions, we have replaced Figures 6 and 7 in the manuscript with Figures R4 and R5, respectively, to include the total primary sources. Please refer to Line 290 and Line 316. Furthermore, we have included Figures R6 and R7 in the Supplement. Please refer to the Figure S13 and Figure S14. Those include the proportion of each major source and the average daily profile of the total daily P(ROx).

Moreover, we have included an explanation in the Lines 277-278 stating, "*Overall, the total primary production rates of ROx in 2022 were 2.34 ppbv h*$^{-1}$*, which is lower than the 2.94 ppbv h*$^{-1}$ *and 2.85 ppbv h*$^{-1}$ *in 2021, as depicted in Figure S13 of the Supplement.*".

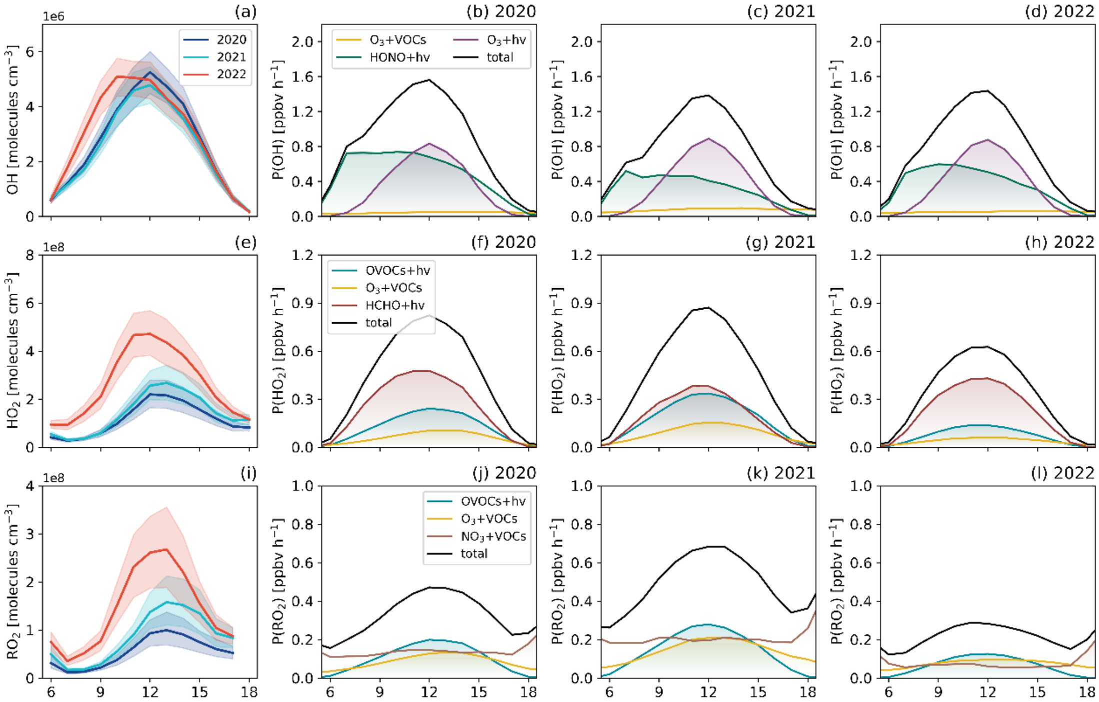

Figure R4. The mean diurnal profiles of simulated OH (a), HO_2 (e), and RO_2 (i) concentrations in 2020, 2021, and 2022. Colored areas denote 95% confidence intervals; The mean diurnal profiles of primary sources of OH radical (b-d), HO_2 radical (f-h), and RO_2 radical (j-l) from model calculations in 2020, 2021 and 2022.

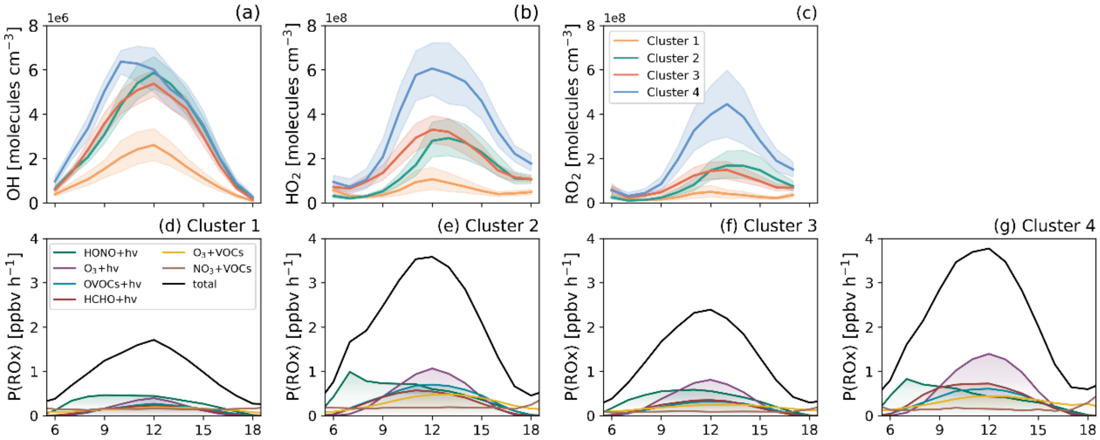

Figure R5. The mean diurnal profiles of simulated OH (a), HO_2 (b), and RO_2 (c) concentrations for Cluster 1, Cluster 2, Cluster 3, and Cluster 4. Colored areas denote 95% confidence intervals; The mean diurnal profiles of primary sources of ROx radical (d-g) from model calculations for Cluster 1, Cluster 2, Cluster 3, and Cluster 4.

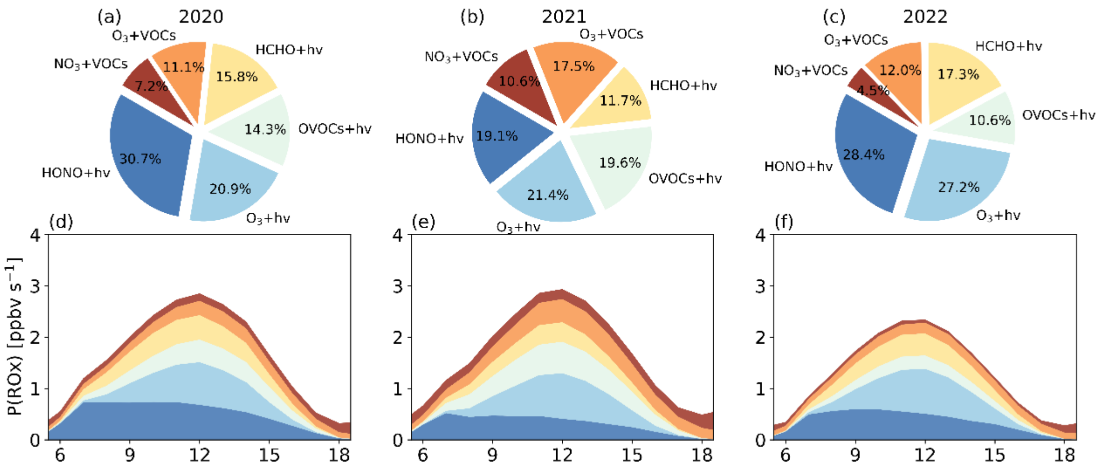

Figure R6. The proportions (a, b, c) and the mean diurnal profiles (d, e, f) of primary sources of daytime radicals during the periods from April to May of 2020, 2021, and 2022.

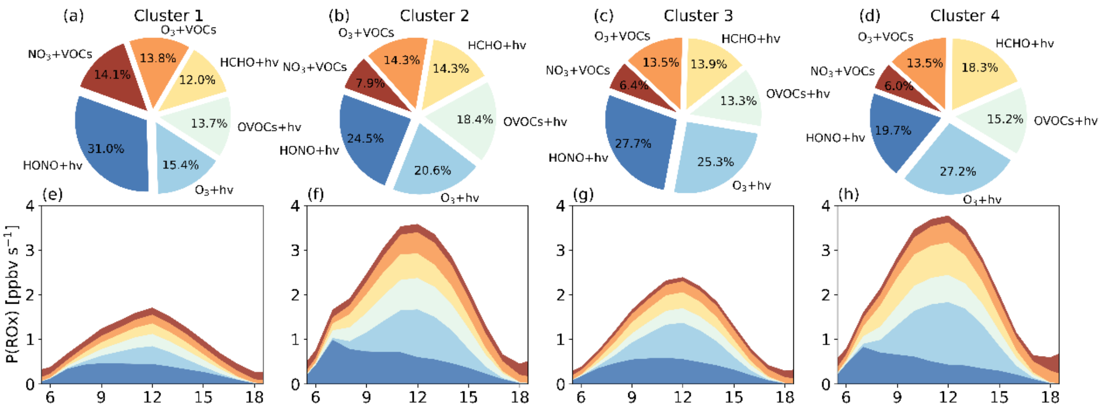

Figure R7. The proportions (a, b, c, d) and the mean diurnal profiles (e, f, g, h) of primary sources of daytime radicals for Cluster 1, Cluster 2, Cluster 3, and Cluster 4.

(7) According to the current analysis, it seems like that the radical chemistry analysis based on the clusters do not really help to explain the high O_3 concentration in 2022, because in line 278-279, it says that:"Cluster 2 and Cluster 4, characterized by significant net ozone production, exhibit distinct features in radical chemistry", however, in 2022, the main clusters are 3 & 4, in addition, in figure 7, the mean diurnal profiles of OH and HO_2 for cluster 3 are always above cluster 4, and even for RO_2, it seems like the average concentrations for RO_2 in cluster 3 and 4 are close by eyes, please check again if there is a big difference of ROx or P(ROx) for cluster 3 and 4.

R: Thanks for your comment. We have characterized the ozone profiles after clustering into four distinct clusters: Cluster 1 with low background concentration and low net production; Cluster 2 with low background concentration and high net production; Cluster 3 with high background concentration and low net production; and Cluster 4 with high background concentration and high net production, as shown in Table R1. Upon statistical analysis, it was found that the number of days with higher average ozone concentrations in Cluster 3 and Cluster 4 increased significantly in 2022 compared to 2020 and 2021.

As shown in Table R1, the reasons for the high average ozone concentration levels in these two clusters were not entirely the same. The high concentrations in Cluster 3 were due to elevated ozone background concentration, whereas in Cluster 4, the high concentrations were attributed to both high background values and high net production. For Cluster 2, it had a high net ozone production but a lower background concentration. Therefore, in the analysis of the primary sources of radicals, Cluster 2 and Cluster 4, which had high net production, exhibited significantly higher primary sources of radicals compared to Cluster 1 and Cluster 3. This suggests from the radical chemistry analysis based on the clusters that a high net production indicates active photochemical processes.

The cluster-based analysis of radical chemistry can explain the high O_3 concentrations observed in 2022. Cluster 4 is characterized by higher concentrations of HO_2 and RO_2 radicals and a higher primary source of radicals. Cluster 3 has moderate levels of radical concentrations and primary sources of radicals, but it features a high ozone background value. The increase in the number of days associated with these two clusters in 2022 has contributed to the elevated ozone levels. Cluster 2 has a higher primary source of radicals, indicating active photochemical processes, but the overall ozone levels are moderate due to the lower background ozone values.

Table R1. The ozone concentration (ppbv) characteristics, the average daytime radicals concentration (molecules cm^{-3}), and the average reaction rates of the main processes for Cluster 1-Cluster 4.

	Cluster 1	Cluster 2	Cluster 3	Cluster 4
O_3 background	22.4	16.9	40.6	33.3
O_3 net production	14.8	45.9	17.5	50.9
OH concentration	1.4×10^6	3.3×10^6	3.1×10^6	3.9×10^6
HO_2 concentration	0.6×10^8	1.5×10^8	1.9×10^8	3.5×10^8
RO_2 concentration	0.3×10^8	0.8×10^8	0.9×10^8	2.2×10^8
P(ROx)	0.92	2.09	1.35	2.23
OH propagation (OH+VOCs)	0.68	1.75	1.16	2.03
OH termination (OH+NO_2)	0.63	1.14	0.69	0.88
propagation/termination	1.08	1.54	1.69	2.29
P(O_3)	3.12	7.73	5.24	8.20

(8) In line 300: "OH oxidation of CO and VOCs produces HO_2 and RO_2", the concentration of CO was not given. And also, the concentration of NO was not given.

R: Thanks for your comment. The CO and NO data you referred to were not observed simultaneously in this study. Consequently, the CO data used in the model was a fixed value of 0.8 ppmv, and the NO data was calculated by the OBM model. This indeed represents a source of uncertainty in the model.

(9) In line 306-308: Specifically, the reactions of OH+NO_2 and RO_2+NO_2 accounted for approximately 0.51 ppbv h^{-1} (0.76 ppbv h^{-1} in 2020 and 0.74 ppbv h^{-1} in 2021) and 0.80 ppbv h^{-1} (0.96 ppbv h^{-1} in 2020 and 1.55 ppbv h^{-1} in 2021) of the ROx radical loss on daytime average, respectively." However, the reaction of RO_2 with NO_2 is generally considered to be not important as the product RO_2NO_2 formed in the reaction of RO_2+NO_2 for R=alkyl or substituted alkyl (but not for R=acyl) will thermally decompose rapidly back to reactants at around room temperature

(Atkinson, R., Atmospheric chemistry of VOCs and NOx. Atmospheric Environment, 2000. 34(12): p. 2063-2101.), does the decomposition reaction of RO_2NO_2 included in the model? This process was not shown in Figure 8.

R: Thanks for your comment. Firstly, the mcm mechanism utilized in the model includes the decomposition reactions of RO_2NO_2. Table R2 displays a selection of these RO_2NO_2 decomposition reactions along with their respective rate constants. Secondly, the manuscript initially described only the reaction rate between RO_2 and NO_2, which could be misleading. Consequently, we have re-evaluated the net production rate of RO_2NO_2, calculated as the generation rate minus the decomposition rate. The findings are now displayed in the revised Figure 8.

Table R2. RO_2NO_2 decomposition reactions involved in MCM mechanism.

reaction rate constant	KD0 = 1.10D-05*M*EXP(-10100/TEMP) ; KDI = 1.90D17*EXP(-14100/TEMP) ; KRD = KD0/KDI ; FCD = 0.30 ; NCD = 0.75-1.27*(LOG10(FCD)) ; FD = 10@(LOG10(FCD)/(1+(LOG10(KRD)/NCD)**2)) ; KBPAN = (KD0*KDI)*FD/(KD0+KDI) ;
reaction equations	% KBPAN : ACRPAN = ACO_3 + NO_2 ; % KBPAN : PAN = $CH3CO_3$ + NO_2 ; % KBPAN : BZEMUCPAN = $BZEMUCCO_3$ + NO_2 ; % KBPAN : TLEMUCPAN = $TLEMUCCO_3$ + NO_2 ; % KBPAN : OXYMUCPAN = $OXYMUCCO_3$ + NO_2 ; % KBPAN : MXYMUCPAN = $MXYMUCCO_3$ + NO_2 ; % KBPAN : PXYMUCPAN = $PXYMUCCO_3$ + NO_2 ; % KBPAN : EBZMUCPAN = $EBZMUCCO_3$ + NO_2 ; % KBPAN : PBZMUCPAN = $PBZMUCCO_3$ + NO_2 ; % KBPAN : IPBZMUCPAN = $IPBZMUCCO_3$ + NO_2 ; …

(10) In addition to the OH-RO_2-HO_2 cycle, which leads to a high production rate of ROx, and the other cycle for OH-HO_2 seems like also be further strengthened in 2022. The average rates for each step related to OH-HO_2 cycle are summarized in the following table according to the model results, it is obvious that reactions for HO_2 + R (R=NO, O_3 and NO_3) → OH and OH + R (R=CO, HCHO) → HO_2 in 2022 with higher rates. Especially for reaction related to O_3, which is 2.6 and 2.1 times faster in 2022 than in 2020 and 2021. Will the OH-HO_2 cycle also help to explain the high ROx or P(ROx) in 2022?

	HO_2+R→OH			HO_2←OH+R	
R	NO	O_3	NO_3	CO	HCHO
2020	2.761	0.047	0.013	1.442	0.225
2021	3.215	0.059	0.013	1.449	0.185
2022	3.352	0.122	0.018	2.108	0.275
2022/2020	1.2	2.4	1.4	1.1	1.2
2022/2021	1.0	2.0	1.3	1.2	1.5

R: Thanks for your comment. The insights you've raised are indeed constructive. As previously mentioned in the text, the report by Volkamer et al. (2010) suggests that approximately 20% of radical production is attributed to the decomposition of closed-shell species, while 80% originates from radical cycles. Upon discovering the improper handling of photolysis data, we reran the model. The table below compiles the average rates for each step related to the OH-HO_2 cycle based on the model's results. The results indicate that in 2022, the reaction rate for OH + R (R = CO, HCHO) → HO_2 was higher, while the rate for HO_2 + R (R = NO, O_3, and NO_3) → OH was lower compared to the years 2020 and 2021. As for reactions related to O_3, the rates in 2022 were 2.4 times and 2.0 times faster than in 2020 and 2021, respectively. We did not observe a more efficient OH-HO_2 cycle in 2022. Moreover, the total P(ROx) in 2022 was the lowest among the three years, yet the ROx concentration was the highest. The relationship between the generation rate and the concentration of products is not a direct cause-and-effect.

We have taken into account the OH-HO_2 cycle in the radical chemistry analysis, and the results of this analysis have been included in the manuscript. Please refer to Lines 332-334.

Table R2. The reaction rates of the main processes in the OH-HO_2 cycle for the three years.

		HO_2+R→OH		HO_2←OH+R	
R	NO	O_3	NO_3	CO	HCHO
2020	3.911	0.052	0.014	1.904	0.309
2021	4.074	0.062	0.015	1.773	0.221
2022	3.435	0.125	0.019	2.086	0.274
2022/2020	0.9	2.6	1.4	1.1	0.9
2022/2021	0.8	2.1	1.3	1.2	1.2

Reference:

Volkamer, R., Sheehy, P., Molina, L. T., and Molina, M. J.: Oxidative capacity of the Mexico City atmosphere-Part 1: A radical source perspective, Atmospheric Chemistry and Physics, 10, 6969-6991, https://doi.org/10.5194/acp-10-6969-2010, 2010.