Response to Reviewers' Comments on Manuscript ID egusphere-2024-3210:
"Observation and modelling of atmospheric OH and HO$_2$ radicals at a subtropical rural site and implications for secondary pollutants"

We sincerely appreciate the editor and the three referees for thoughtful comments and valuable suggestions which has helped us to improve our manuscript. In response to your comments, we have undertaken a comprehensive revision of the manuscript.

Please find our itemized responses below and revisions in the re-submitted files. We use *italicized* text for your questions, **blue** for our response, and red to indicate where changes have been made in the manuscript. The changes inside the manuscript will be highlighted <mark>in yellow</mark>.

Reviewer 2

This manuscript details measurements of OH and HO$_2$ radicals made using a CIMS instrument at a subtropical rural site near the Pearl River Delta in China. These measurements are presented along with radical concentrations from a box model featuring the Master Chemical Mechanism v3.3.1. In general, when constrained to a suite of measured trace gases and meteorological parameters, the model overpredicted the measured radical concentrations, especially during warmer, more polluted periods. The authors also use an additional model, further constrained to the measured radical concentrations, to illustrate that the overprediction of HO$_x$ species results in a significant overestimate of the production rates of secondary pollutants such as ozone and nitric acid.

Accurate field measurements of OH and HO$_2$ are extremely challenging, and the results presented in this manuscript are important to characterizing radical chemistry and the overall oxidative capacity of the atmosphere. While it is clear that a significant amount of work went into the field measurements described in this study, a lack of detail regarding the instrumentation and calibration procedures and limited discussion surrounding the model overestimation of the measured HO$_x$ concentrations limits the conclusions that can be drawn from the results. The strength of the manuscript would be greatly improved if the authors expanded sections 3.2 and 3.3 and offered insight into potential explanations for the discrepancies between measured and modeled HO$_x$ concentrations.

Response: Thank you for your thoughtful review, we have improved the sections on instrumentation, calibration and result discussion. We have responded to your comments in detail under each question.

More specific comments are included below:

Q1: *Section 2.2 – There are few details on the calibration procedure for OH and HO$_2$. Given the importance of the calibration factor for each species, a brief description of the process should be included. The authors do describe that equivalent amounts of OH and HO$_2$ are produced by the calibration source – is the residence time of radicals in the calibration source sufficient such that wall interactions and radical-radical loss*

mechanisms must be considered to determine the concentrations of OH and HO₂ that exit the calibrator and enter the sampling inlet?

Response:

Thanks for the comments. The detailed procedures on calibration were added to the SI and shown in the previous response (refer to referee 1 Q2). The calibration unit and setup are similar to the one developed by Kürten et al. (2012). In this calibration unit, the proximity of the calibration lamp to the sample inlet (less than 1 cm) and the swift transition of radicals from the front injector (1 cm away) (refer to Figure S6a as shown below) gives a residence time of less than 20 ms. This short residence time, combined with the laminar flow conditions in the calibrator and inlets (Reynolds Number < 2000), effectively negates the potential for significant radical-radical loss and wall interactions. Thus, the wall loss and radical-radical loss between source and conversion zone is believed negligible.

Revision in Text S4.1 on page 10-11 of the SI:

"Furthermore, the potential for radical-radical loss after radicals exit the calibrator and enter the sampling inlet was considered. Given the flow speed of the ambient inlet (12.2 m/s), the sample inlet (55 cm/s), and the distances involved—the calibration lamp is less than 1 cm from the sample inlet, and the sampling port to the front injectors is 1 cm—it can be calculated that the transport time for radicals to the front injectors for reactions is less than 20 ms. This brief transport time is sufficiently short to prevent significant radical-radical losses. Additionally, since the sample inlet draws the central part of the airflow within the ambient inlet, and the flow in the sample inlet is laminar, wall losses at this stage are also considered negligible."

Besides, triggered by the reviewer's comment on wall loss in the calibration unit, we also discussed possibility of loss of OH and HO₂ in the ambient inlet on Text S4.1 on page 10 line 6 of the SI, as below.

"Wall losses in the ambient inlet were evaluated by varying the distances of the calibration lamp from the inlet to assess potential effects on signal attenuation. The instrument was calibrated in two distinct configurations: initially, the lamp was positioned close to the CIMS sample inlet (Figure S6a, and subsequently, moved away from the CIMS sample inlet (Figure S6b. By comparing the observed signals from these two configurations, we were able to calculate the wall losses associated with the ambient inlet. The results indicated no significant difference (<1%) between the two measurements, suggesting negligible wall losses in the sampling system. "
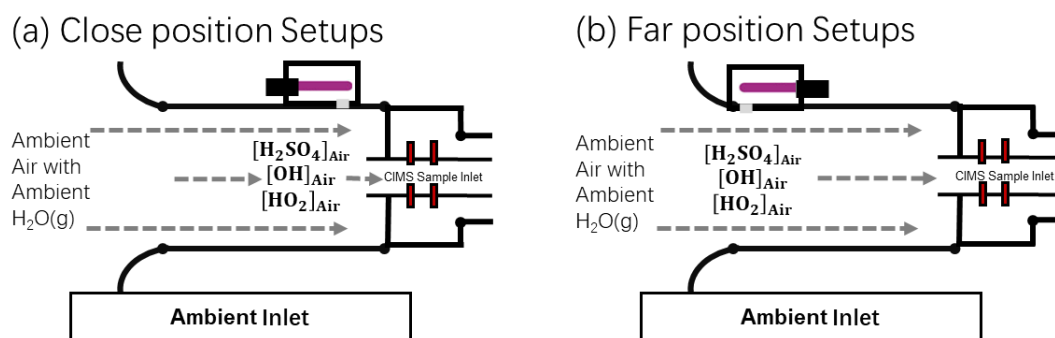
Figure S8 the calibration process during ambient sampling in (a) close and (b) far positions.

Q2: *Section 2.2 and Table S3 – Similar to above, there are limited details regarding the timing of the measurement sequence and the addition of the scavenger gas. The manuscript should not describe the OH, HO₂, and H₂SO₄ measurements as simultaneous but should instead detail the amount of time spent in each measurement mode. In the main text, the authors also describe that OH and HO₂ concentrations are derived from a simple subtraction of background signals, while Table S3 lists the scavenging efficiency for OH and HO₂. How are these scavenging efficiency values determined and how are they factored into the determination of radical concentrations? Are there any lingering effects of the scavenger gas that must be considered similar to the residual NO that is described in Text S2? These details would provide additional confidence in the radical measurements.*

Response: Thank you for your inquiry. The duty cycle for our CIMS were 6 minutes for HO$_2$, 4 minutes for H$_2$SO$_4$, and 50 minutes for OH, alternating between 1 min measurement model and 1 min background mode. The scavenger efficiency for OH and HO$_2$ are 100%. The lingering effect of scavenger gas is negligible (see detail discussion below).

We have included a detailed duty cycle on page 13 to 14 in the Supplementary Information (Text S5, Tabel S6 and Figure S6) of the revised manuscript as below:

"As detailed in Section 2.2, the PolyU-CIMS was configured to sequentially measure HO$_2$, H$_2$SO$_4$, and OH within each hour during the field study, corresponding to changes in injection gases. Table S3 outlines the hourly schedule and injection gases Figure S9 a 1-hour duty cycle.

Table S6 Duty cycle and injection gases for targeted chemical analysis.

Purpose	Measurement Mode	Signal 97 Label	Chemicals injected to the sample flow through different injectors		Duty time (s)	Repeat times	Total Duration (mins)
			Front Injectors	Rear Injectors			
HO$_2$	SIG	S$_{97NO}$	NO, N$_{2(p)}$, SO$_2$,	Sca, Sca$_{(p)}$	60	3	6
	BKG	S$_{97NOSca}$	NO, Sca$_{(p)}$, SO$_2$	Sca, N$_{2(p)}$	60		
H$_2$SO$_4$	SIG	S$_{97w/o}$	-	Sca, Sca$_{(p)}$	60	2	4
	BKG	S$_{97w/o}$	-	Sca, N$_{2(p)}$	60		
OH	SIG	S$_{97SO2}$	N$_{2(p)}$, SO$_2$,	Sca, Sca$_{(p)}$	60	25	50
	BKG	S$_{97SO2Sca}$	Sca$_{(p)}$, SO$_2$	Sca, N$_{2(p)}$	60		

Notes:

Front and Rear Injectors - The injector pairs as demonstrated in the Figure S2

SIG & BKG – the signal and background modes.

Sca - scavenger gases, C$_3$F$_6$ in this study.

Sca$_{(p)}$ - scavenger gases, add through the pulsed flow

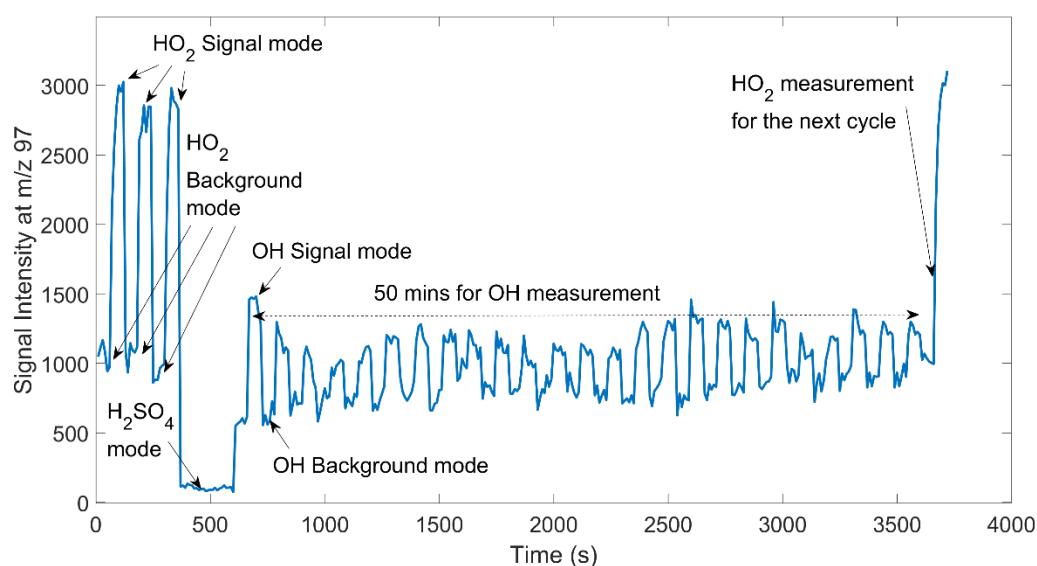N$_{2(p)}$- nitrogen gases, add through the pulsed flow

Figure S9 Variation of signal intensity at m/z 97 during a 1-hour duty cycle of CIMS measurement.”

Regarding to referee's comment on lingering effects of scavenger gas, our tests showed it is negligible in our CIMS. Details added on page 9 line 20 of the SI in revised manuscript (Test S3 and Figure S7):

“In our setup, there is residual C$_3$F$_6$ present after CIMS switches from background to signal mode, but it does not affect the measurement results. As shown in Figure S7, after switching off C$_3$F$_6$, the measurement signals rapidly return to their initial levels within 20 seconds. Data affected by C$_3$F$_6$ residual are excluded to minimize the impact of the residual C$_3$F$_6$ on the measurements.
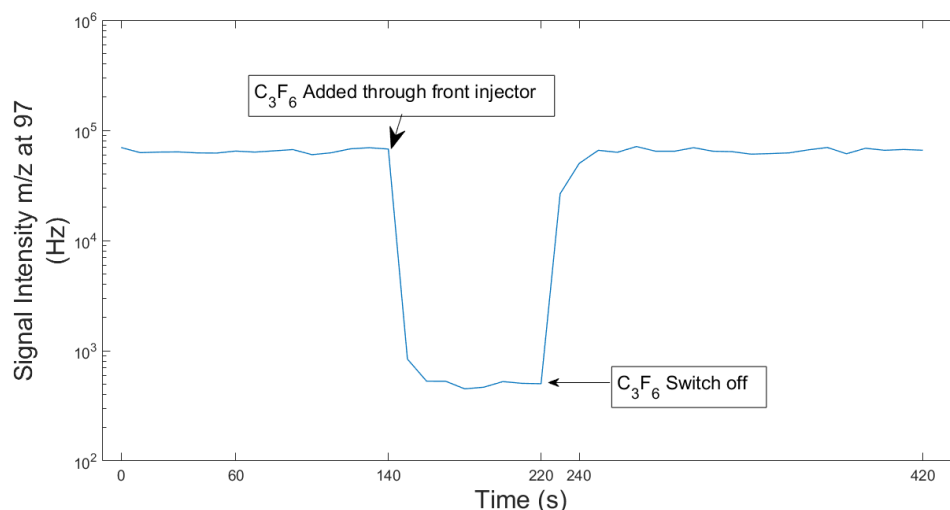
Figure S7 Variation of signal intensity m/z at 97 before C_3F_6 addition with time, after addition and switching off of C_3F_6 in synthetic air containing OH of $\sim5\times10^8$ cm^{-3}."

Q3: *Page 8, Line 11. After this description of HO_2 uptake on aerosols, this process is not included as a loss mechanism in Figure 5 or discussed in the remainder of the manuscript despite SMPS measurements of particle size and number being shown in Figure 3. Is this uptake negligible compared to other loss mechanisms shown in Figure 5? Is RO_2 loss on aerosols also included in the model?*

Response: Thank you for your comment. The heterogeneous uptake of HO_2 on aerosols was included in our model with minor contribution to the loss of HO_2. But it was not shown in Figure 5 in the previous version. In the updated manuscript, we have revised this figure to include this process as a loss mechanism, indicating insignificant uptake of HO_2. We have clarified this in the updated manuscript. The losses of RO_2 on aerosols are not considered in our model.

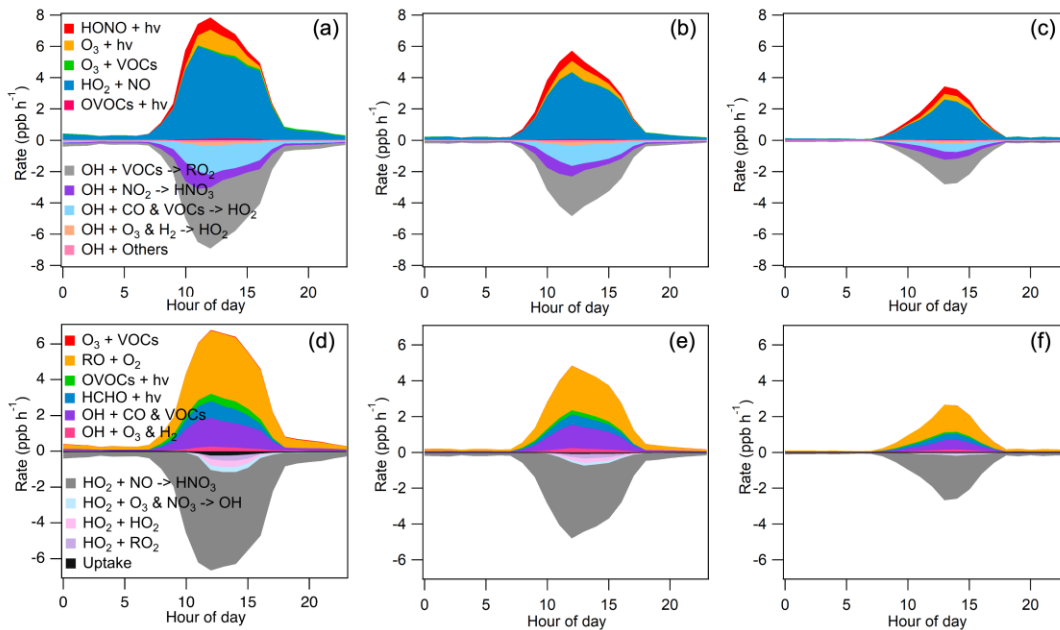Revised Figure 6 (Figure 5 in previous version) on page 15:

"

Figure 6 Chemical budgets of OH and HO_2 for PRD (a, d), CEC (b, e), and CNC (c, f) simulated using a chemical box model."

Revised section 3.2 on page 15:

"The sinks of HO_2 varied among the cases with minor contribution from the uptake process, driven by radical termination mechanisms. The rate of radical self-reactions decreased from PRD to CNC."

Q4: *Page 16, Lined 7-15: As mentioned above, the significant overprediction of OH and HO_2 during the PRD and CEC should be the main focus but the current manuscript offers very little in the form of discussion. I suggest expanding this section to include the rate of HO_2 loss necessary to account for the difference between modeled and measured concentrations, how this rate compares to other processes shown in Figure 5, and potential explanations for the discrepancies.*

Response: We agree that the overestimation of radicals should be a key focus of the manuscript. Following the reviewer's suggestion, we reviewed the literature and conducted model sensitivity tests to explore potential causes. In brief, the overestimation of HO_2 at PRD may result from missing HO_2-to-OH conversion processes. For the CEC air mass, we hypothesize that the overestimation of OH and HO_2 is primarily due to radical terminal reactions and limited measurements of OVOCs in this air mass which was strongly influenced by vehicular emissions. The detail and lengthy discussions have been added in the revised version and made on pages 19–21 as shown below:
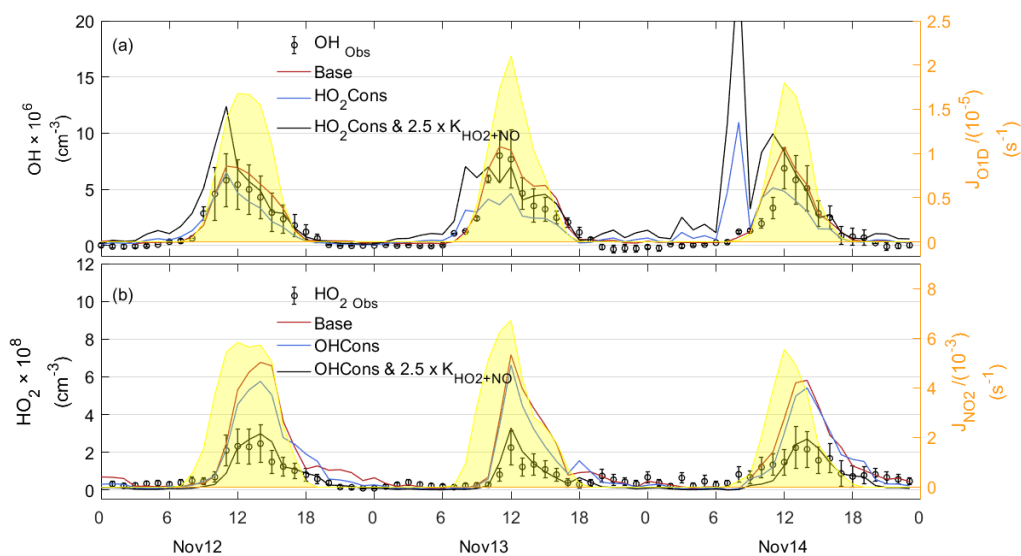
Revised section 3.3.1 to 3.3.2 on page 17 to 19:

"

Figure 7 observed and simulated time series of OH and HO$_2$ for the PRD case. The "Obs" subscript denotes the observation data. "Base" denotes the result of Baseline scenario as described in Box Model section. "Cons" denotes the results with additional constrained species compared to Base. "2.5 × K$_{HO2+NO}$" denotes the results with increasing the reaction rate coefficient of R11 by a factor of 2.5.
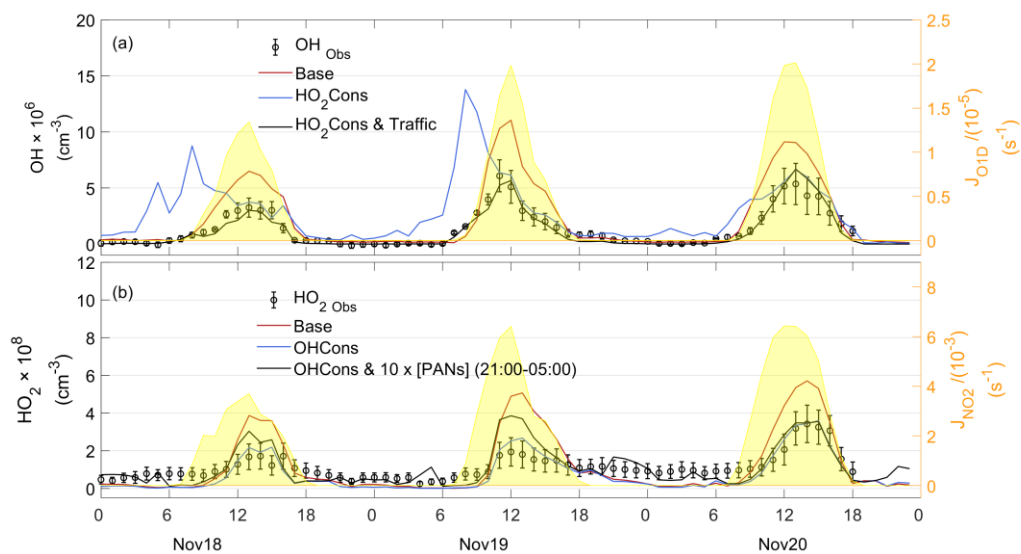

Figure 8 observed and simulated time series of OH and HO$_2$ for the CEC case. The "Obs" subscript denotes the observation data. "Base" denotes the result of Baseline scenario as described in Box Model section. "Cons" denotes the results with additional constrained species compared to Base. "Traffic" denotes the sensitivity test results with consideration of vehicular emission (see Test S7 in SI). "10 × [PANs] (21:00-05:00)" denotes the results with increasing nighttime secondary concentration of PAN by a factor of 10.
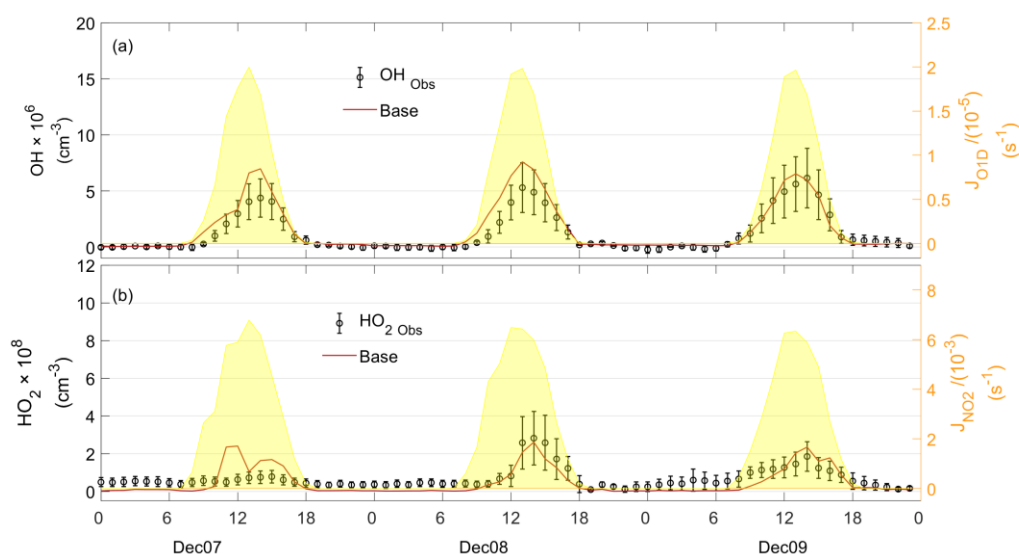
Figure 9 observed and simulated time series of OH and HO_2 for the CNC case. "Base" denotes the result of Baseline scenario as described in Box Model section.

3.3.1 Substantial overestimation of HO_2 in PRD case

To explain the HO_2 over-simulation by the base model, we constrain OH or HO_2 and compared it to the base case (without constraining OH and HO_2). Result shows that constraining HO_2 causes the model to underestimate OH (blue line in Figure 7a), while constraining OH leads the model to still substantially overestimate HO_2 (blue line in Figure 7b). This result suggests that aligning the modeled OH and HO_2 with observations may require introducing a strong, unknown process for HO_2 that efficiently recycles OH with a high yield (Kanaya et al., 2012). A sensitivity analysis shows that increasing the reaction rate coefficient of $HO_2 + NO \rightarrow OH + NO_2$ (R11) by a factor of 2.5 would largely reduce both the HO_2 overestimation and the OH underestimation as shown by the black line in Figure 7. However, it is not clear what such OH cycling reaction is. Thus, the exact cause of the overestimation of HO_2 in the PRD case remains unresolved.

3.3.2 Moderate overestimation of both OH and HO_2 radicals in CEC case

Unlike the PRD case, constraining either OH or HO_2 in the CEC case generally reduces the daytime overestimation of both HO_2 and OH. These results indicate an additional sink for both OH and HO_2, as suggested by Bottorff et al. (2023). However, the OH concentration shows an overestimation in the morning when HO_2 was constrained, which may suggest missing OH reactivity in the morning. To further investigate the underlying causes, we examined the correlations between various pollutants. The significant negative correlation between CO and NO ($R^2=0.49$, $p=0.01$, Figure S6b)

suggests that CEC in the morning may have been influenced by emission from fresh complete combustion during the CEC case, whereas such correlations for PRD and CNC are not significant (Figure S6a and c). This indicates that the missing OH reactivity of CEC in the morning is possibly related to fresh vehicle emissions.

Diesel vehicle exhausts are rich in OVOCs relative to total VOCs (Yang et al., 2023). In our study, OVOCs were measured, except formaldehyde and acetaldehyde. We conducted a sensitivity analysis by adding these two OVOCs in the model (see Text S7 for details). After accounting for their influence, the overestimation of OH in the morning with constraining HO_2 could be significantly reduced (Figure 8a black line).”

Revised Text S7 on page 14 to 15 of the SI:

“A sensitivity test was conducted for the CEC case to account for the missing OH reactivity in the morning. This missing OH reactivity was attributed to unmeasured species in the fresh diesel exhaust. To estimate this, we first calculated the total OH reactivity of the exhaust based on the reactivity of NO_x and CO, along with the diesel exhaust source profile. The contributions from NO_x and CO were then subtracted. The remaining OH reactivity was allocated to formaldehyde and acetaldehyde, with their concentrations adjusted accordingly. This allocation was justified by the significant contribution of OVOCs to the total reactivity of diesel exhaust (Yao et al., 2015; Mo et al., 2016), as formaldehyde and acetaldehyde were not measured in this study. The sensitivity test was performed following these steps:

1. First, we calculated the OH reactivity of freshly emitted NOx and CO at each time step. We assumed that the pollutant concentrations at the time of the highest NO concentration did not undergo significant photochemical loss. For each time step, we calculated the ratio of the OH concentration at the time of the highest NO concentration to the OH concentration at that time step. This ratio was then multiplied by the OH reactivity of ambient NO_x and CO at that time step to estimate the OH reactivity from the emitted NO_x and CO.

2. The observed exhaust OH reactivity was determined by dividing the OH reactivity of emitted NO_x and CO by 20%, which represents the minimum contribution of NO_x and CO to the observed OH reactivity in exhaust in China (Yang, 2023).

3. The total exhaust OH reactivity was derived by dividing the observed exhaust OH reactivity by 60%, to account for the approximately 40% of OH reactivity missing in Chinese diesel exhaust (Yang, 2023). The OH reactivity of emitted NO_x and CO was then subtracted from the total exhaust OH reactivity.

4. The remaining OH reactivity was allocated to formaldehyde and acetaldehyde in a 1:1.6 ratio, and their concentrations were adjusted accordingly. This ratio was calculated based on the concentration ratios of formaldehyde and acetaldehyde in diesel exhaust (Yao et al., 2015) and their respective OH reactivity coefficients.”

Q5: *Figure 6: While the more significant discrepancies during the daytime should be the focus of the discussion, the model also underestimates HO$_2$ at night during CEC and CNC. This should also be mentioned in the manuscript and could be added to the discussion.*

Response: We speculate that the under-simulation of nighttime HO$_2$ is in part due to an underestimation of PAN concentrations by the model. However, other unknown processes must have a large contribution. We added a sensitivity test and discussion in section 3.3.3 on page 19 of the manuscript:

"**3.3.3 Nighttime underestimation of HO$_2$ in CEC case**

Ozone and NO$_3$ reactions with alkenes can produce HO$_2$ at night (Walker et al., 2015). In our study, alkenes are unlikely to be the main cause for the underestimation because the major alkenes were measured, and the alkenes concentrations in the CEC case were much lower compared to the PRD case in which no underestimation of nighttime HO$_2$ was found. A previous study (Whalley et al., 2010) showed that nighttime HO$_2$ underestimation at a clean tropical Atlantic site was significantly reduced by constraining the model with higher PAN. In our study, PAN was not measured. The model simulated nighttime PAN mixing ratios (0.1-0.7 ppb) were lower than previous observed nighttime results in the coastal (up to 1 ppb) (Xu et al., 2015) and mountain site (up to 2 ppb) (Wang et al., 2023) in southern China. To assess the impact of PAN concentration on nighttime HO$_2$ levels, a sensitivity analysis was conducted in which the PAN concentration was increased. The results show that only when the PAN concentrations were increased by tenfold, the model simulated nighttime PAN level could match the observations (Figure 8b, black line). This suggests that underestimated PAN might have contributed to the model's nighttime HO$_2$ underestimation, but other processes must have a larger contribution."

Q6: *Figure 3 and Section 3.1.2 – I suggest highlighting the different measurement periods in Figure 3 to better communicate which observations are included in the PRD, CEC, and CNC periods. At first glance, it appears that the majority of the highest observed HO$_x$ concentrations occurred during the three cases, and the lowest HO$_x$ concentrations (December 1-6 and 10-19) are omitted from the analysis. Were model runs also performed for these days?*

Response: Thank you for your suggestion. We have marked the different periods for the PRD, CEC, and CNC cases in Figure 3 in revised manuscript. On selection of CNC cases. We selected the three days with the highest and most consistent solar radiation for cases analysis. Other CNS cases with lower solar radiation (December 1-6 and 10-19) were not further analyzed.

We have added descriptions on the Section 3.1.2 on page 13 as follow:

"For each phase, a representative three-day period was selected for detailed analysis based on the availability of comprehensive data and sunny conditions (colored trajectories in Figure 4)."

Q7: *Figure S6: The standard deviation of AVOC and OVOC measurements increases suddenly during the daytime in the PRD case. Is it possible that the short gap in VOC measurements shown in Figure 3 is included in the average?*

Response: The increases of standard deviation of AVOCs and OVOCs in PRD are due to the missing data on afternoon of November 14th and the large variation between data collected on afternoon of November 12th and November 13th. Additionally, we decided to add Figure S6 to the main content (Figure5 in the new version) to provide diurnal variations information in the revised manuscript. We have added a detailed explanation of this occurrence to the Figure 5 captions and provide context to the observed data patterns on page 14:
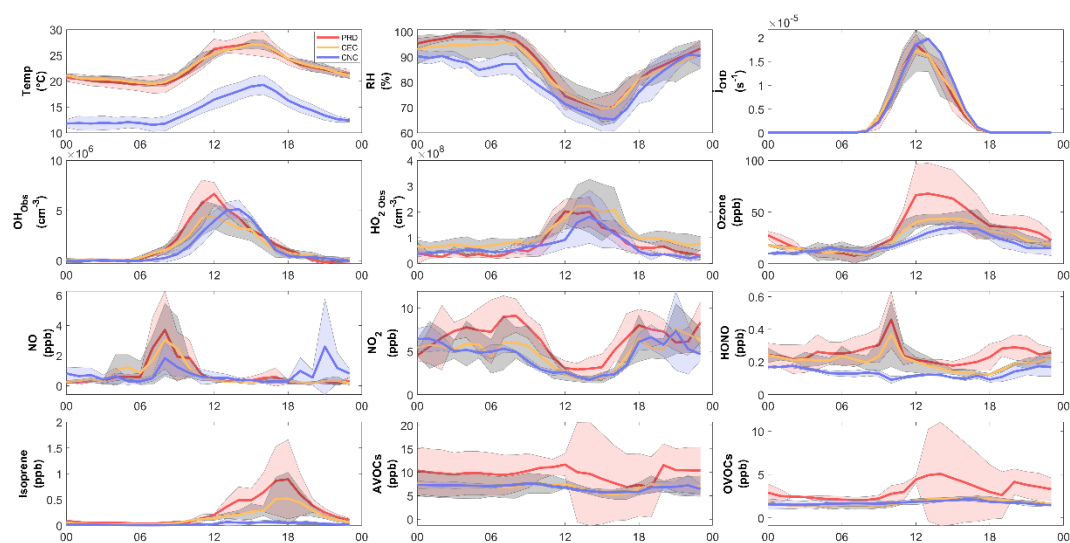
"

Figure 5 Average diurnal variations of (a) Temperature (b) Relative Humidity (c) J_{O1D} (d) OH (e)HO$_2$ (f) Ozone (g) NO (h) NO$_2$ (i)HONO (j)Isoprene (k) AVOCs (l) OVOCs. The solid-colored lines represent selected cases: orange for PRD, green for CEC, and blue for CNC. The light band represents the standard deviations of the mean. The increase in the standard deviations of VOCs and OVOCs during the PRD case is a result of absence of data on the afternoon of November 14th and large variations in on November 12th and 13th."

Minor comments:

Q8: *The instrument to measure HONO is not listed in Table S2*

Response: We have updated Table S2 to include the instrument (LOPOP-03) used for HONO measurement on page 5 of the SI.

Q9: *Figure 5: The y-axis label should be ppb h^{-1} not ppb s^{-1} and OH + NO$_2$ should form HNO$_3$. In general, this figure is not easy to interpret due to the different axis scales and very small colored sections relative to reactions with NO. A total radical (RO$_x$) budget that does not include propagation channels may better illustrate the relative importance of initiation and termination processes in the model.*

Response: Thank you for pointing this out. The suggested revisions have been incorporated into Figure 6 (Figure 5 in previous version) on page 15 of the manuscript. Regarding the inclusion of a total radical (RO_x) budget, we note that due to the absence of direct measurements for RO_2, we lack a solid analytical basis to construct a reliable RO_x budget. Therefore, we have not incorporated this metric, focusing instead on the OH and HO_2 we have measured and analyzed.

Q10: *Figure S4: As all data from the campaign is averaged together, this figure is misleading for some species that vary significantly from November to December such as isoprene or HONO. I suggest separating the data into two or three averaging periods or combining this figure with Figure S6 to illustrate how HONO, isoprene, and ozone changed during the transition from PRD to CEC and CNC.*

Response: In the revised Figure 5 (Figure S6 in previous version), we now present the average values for each of the three periods, addressing the significant variability of certain species like isoprene and HONO from November to December. This adjustment ensures a more accurate representation of how these species, along with ozone, vary during the transition from PRD to CEC and CNC.

Q11: *Tables 1, S2, and S4: Aligning text to the left of each column would improve readability. There is also a problem with the resolution of Table S2.*

Response: We have accepted the suggestion and improved the readability of Tables 1, S2, and S4 by aligning the text to the left in each column on page 11 to 12 of the manuscript, page 5 and page 7 of the SI, respectively.