Response to Reviewers' Comments on Manuscript ID egusphere-2024-3210:
"Observation and modelling of atmospheric OH and HO₂ 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 in yellow.

Reviewer 1

The study presents valuable measurements of OH and HO₂ radicals using the CIMS technique at a subtropical rural site in southern China during November and December 2022. The data suggest generally lower concentrations of OH and HO₂ compared to previous studies. By categorizing the data into three distinct cases based on backward trajectory analysis, the study highlights good agreement between observations and model predictions under cold, clean conditions but significant overestimation under warm, polluted conditions. This overestimation, which affects secondary pollutant production, underscores the need for further investigation into HO_x sources and sinks to resolve model-observation discrepancies. While this study provides valuable insights into HO_x radical behavior in a subtropical rural environment, several aspects require clarification and deeper discussion. Addressing these issues will strengthen the study's conclusions and enhance its contribution to understanding radical chemistry and secondary pollutant formation in rural and polluted environments. Below are detailed comments.

Response: Thanks very much for the constructive comments. Following your suggestions, we have revised the manuscript.

Q1: *The introduction section needs more comprehensive referencing. Important studies in the field of HOx radical chemistry, particularly those relevant to subtropical and rural environments, should be cited to provide better context and demonstrate the study's relevance.*

Response: We have incorporated additional references on HO_x radical chemistry in subtropical and rural environments into the introduction, results and discussion sections. Additionally, we have revised some descriptions to better provide context and highlight the relevance of our study.

Revision on pages 2-3: "Previous studies have shown that models generally predict OH levels well in polluted conditions (NO > 1 ppb), but notable overestimation were observed under low NO and aged conditions, such as coastal areas (Kanaya et al., 2007; Zou et al., 2023), marine boundary layers (Berresheim et al., 2002; Carslaw et al., 1999), and the rural area (Bottorff et al., 2023; Kanaya et al., 2012). Missing OH sinks from

both measurement or chemical mechanism were proposed as the primary reason for the overestimation (Lou et al., 2010; Yang et al., 2016; Hansen et al., 2014 Thames et al., 2020). Underestimation of OH concentrations were also observed in high biogenic VOCs (BVOCs) and low NO (<1 ppb) conditions which generally happen in the subtropical or tropical area (Hofzumahaus et al., 2009; Lelieveld et al., 2008; Tan et al., 2001; Whalley et al., 2011)……Those results called for more measurement and modelling in the subtropical and tropical rural areas. "

Revision on page 16: "The modeled and observed concentrations of OH and HO_2 radicals were compared to evaluate the performance of the model. In the PRD case (Figure 7), which is the most polluted and warmest among the three cases, the OH concentration was only slightly overestimated, whereas the HO_2 concentration was substantially overpredicted by the model during the daytime. Similar result has been observed at another rural site (Kanaya et al., 2012). For the CEC case (Figure 8), the model moderately overestimated both radicals during the daytime but underestimated the nighttime HO_2 concentration, which is similar to the findings at a rural forest site (Bottorff et al., 2023). In the CNC case (Figure 9), the model results were generally within the measurement uncertainty, with some daytime overestimation of HO_x on December 7 (similar to the PRD case) and nighttime underestimation of HO_2 (similar to the CEC case). In the following section, we conduct sensitivity tests to explore the possible reasons for the model observation discrepancy in the PRD and CEC cases."

Revision on page 18 line 9: "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)."

Q2: *The calibration procedures for OH and HO_2 require further clarification. Given the critical role of the calibration factor in determining OH concentrations, a detailed explanation of the calibration methodology is essential.*

Response: We have added more details on OH and HO_2 calibration to the Supplementary Information (SI).

Revision in Text S1 on page 8 of the SI: "The calibration of Chemical Ionization Mass Spectrometer (CIMS) involves the generation of OH and HO_2 radicals through photolysis of water vapor by 184.9 nm light, as outlined in Reaction R30. The concentration of radicals produced during calibration is determined from the known concentration of water vapor [H_2O], which is calculated from water vapor pressure and the relative humidity and temperature. Other essential parameters include the photolysis cross-section of water vapor ($\sigma_{H2O} = 7.14 \times 10^{-20}$ cm^2; Cantrell et al., 1997), the photolysis quantum yield (Φ, assumed to be 1, Kürten et al., 2012) and the photon flux (*It* value, see details about *It* value determination on Kürten et al., 2012). The generated radical concentrations ([OH] and [HO_2]) are calculated using the following equations:

$$[OH] = [HO_2] = [H_2O] * \sigma_{H_2O} * \Phi * It$$

From these values, the calibration factors for OH and HO_2 (C_{OH} and C_{HO2}) are calculated using the signals obtained during calibration (S_{OHcal} and S_{HO2cal}), as expressed in the transformed equations E1 and E2:

$$C_{OH} = \frac{1}{[OH]_{cal}} \times \frac{S_{OHcal}}{S_{62}} \text{ (E1, transformed)}$$

$$C_{HO2} = \frac{1}{[HO_2]_{cal}} \times \frac{S_{HO2cal}}{S_{62}} \text{ (E2, transformed)}$$

The calibrator produced OH and HO_2 concentrations in the range of 3×10^7 to 1×10^9 cm^{-3} depending on RH conditions in 10 LMP synthetic air. The more detailed information on calculation procedures is given in our previous study (Zou et al., 2023).

Q3: *The manuscript should specify the scavenge efficiency of OH during the measurement process. How was it ensured that OH radicals were entirely removed? This information is crucial to validate the reported OH concentrations.*

Response: The scavenge efficiency of OH is 100% in our system. This is achieved by increasing the scavenger gas (C_3F_6) amount to the level at the OH signal stopped decreasing during calibration. Any remaining signals are attributable to instrument noise, which includes potential contributions from Criegee intermediates and ambient sulfuric acid, rather than residual unscavenged radicals.

Besides, the terminology of "scavenge efficiency" we used in Table S4 may unintentionally implies incomplete removal of OH and HO_2 radicals. We have revised them to "background to signal ratio (B/S Ratio)" to more accurately reflect that the residual signals are measures of background noise rather than incomplete scavenging.

Revision in Text S3 on page 9 line 15 of the SI: "To determine the amount of C_3F_6 that is needed to achieve complete OH scavenge, we gradually increased C_3F_6 added to high concentrations of OH and HO_2 ($[HO_x] \approx 10^9$ cm^{-3}) generated from the calibrator in synthetic air until no further reduction in the measured signal, which indicates complete scavenging of OH. This point defines the background noise which is attributed to any Criegee intermediates and ambient sulfuric acid."

Q4: *The efficiency of HO_2 conversion via its reaction with NO should be discussed in detail. Is the conversion complete, or is it assumed to operate at a constant efficiency? This factor significantly affects the accuracy of HO_2 measurements.*

Response: Based on the laboratory tests, the conversion of HO_2 to OH by NO and further to H_2SO_4 for detection is 100% ($[H_2SO_4]/[HO_2] = 1$). We assume similar complete (and constant) conversion in the ambient air because the added conversion gases overwhelm the ambient concentrations (~500 times higher) in our study site.

Revision in Text S2 on page 10 of the SI: "

"During HO_2 measurement, ambient HO_2 converted from NO to OH. It should be noted that in HO_2 mode, the increasing NO concentration can enhance HO_2 conversion to OH

(R11), but excessive NO levels trigger the HONO formation when reacts with OH (R15), competing with the OH conversion process by SO_2 (R21) and lowering the detection efficiency for OH. Consequently, the NO to SO_2 concentration ratio is crucial for HO_2 measurements. Sensitivity tests revealed an optimal $[NO]/[SO_2]$ ratio of 0.1 for the PolyU-CIMS and 100% conversion of HO_2 in the laboratory ($[H_2SO_4]/[HO_2] = 1$), aligning with prior research recommendations (Edwards et al., 2003; Sjostedt et al., 2007). Because the concentrations of both SO_2 and NO injected to sample flow are maintained at levels over 100-1000 times higher than those in the ambient atmosphere and the injection flow rates are fixed, the efficiency of the HO_2 to OH conversion remains stable and is believed to be at completion."

Q5: *The manuscript should elaborate on the HO_2 titration process, specifically how HO_2 is converted to OH and subsequently reacts with C_3F_6. The scavenge efficiency for this step may differ from that of OH, which could influence the accuracy of HO_2 measurements.*

Response: As responded to Q4, HO_2 was converted to OH at 100% by adding high concentrations of NO. The HO_2 converted OH was scavenged by C_3F_6 in the same way as for the OH mode (see the response to Q3). The C_3F_6 concentration that achieved 100% scavenging of OH from HO_2 conversion was adopted in both OH and HO_2 modes to ensure complete scavenging OH in the two modes.

To further elaborate on the background measurement process, we have added the following detailed description in Text S3 on page 10 of SI the revised manuscript:

"In the background mode, scavenger gases C_3F_6 are introduced into the sample flow along with SO_2. Given that the concentration of C_3F_6 is 100 times higher than that of SO_2, the ambient OH and any ambient HO_2 converted to OH are scavenged by C_3F_6, rather than being converted to H_2SO_4 for further detection. As a result, in background mode, we are able to accurately determine the interference signals."

Q6: *The unit of the calibration factor should not be expressed as 'cm^{-3}.' This error needs correction for consistency and clarity.*

Response: The appropriate unit should be cm^3 this has now been corrected throughout the manuscript.

Q7: *The manuscript claims a measurement accuracy of 44% for HO_2 and 46% for OH. However, this discrepancy is counterintuitive and should be explained, as HO_2 measurements are typically less accurate than OH measurements.*

Response: The reported accuracies for OH and HO_2 were mistakenly reversed in the initial submission. This has been corrected in the revised manuscript, with 44% for OH and 46% for HO_2.

Q8: *Previous studies in rural areas generally report underestimation of OH and HO_2, yet this study finds significant overestimation under certain conditions. This*

discrepancy requires further discussion, especially concerning the chemical mechanisms and environmental factors leading to such outcomes.

Response: The previous studies found instances of good agreement, overestimations and underestimations in similar studies. We have summarized these discrepancies in the Introduction and Discussion section of the revised manuscript and gives detailed discussion on possible explanations on section 3.3.1 to 3.3.3 respect to different scenarios. For the revisions on the Introduction section please refer to Q1.

Rewrite discussion on page 16:

"The modeled ……Similar result has been observed at another rural site (Kanaya et al., 2012). For the CEC case (Figure 8), the model moderately overestimated both radicals during the daytime but underestimated the nighttime HO_2 concentration, which is similar to the findings at a rural forest site (Bottorff et al., 2023). In the CNC case (Figure 9), the model results were generally within the measurement uncertainty, with some daytime overestimation of HO_x on December 7 (similar to the PRD case) and nighttime underestimation of HO_2 (similar to the CEC case). In the following section, we conduct sensitivity tests to explore the possible reasons for the model observation discrepancy in the PRD and CEC cases."

Additional figures and discussion on page 17-19:
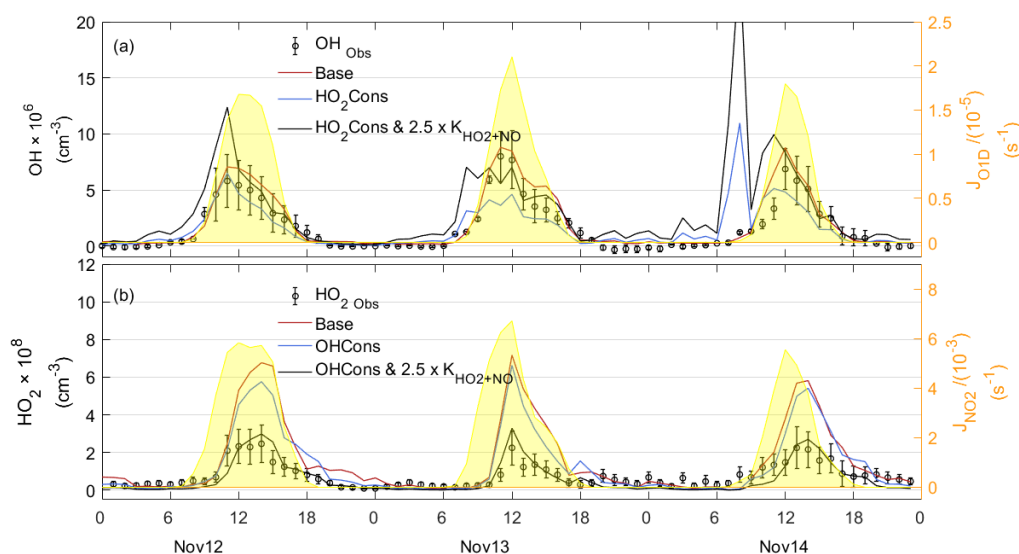
"**Figure 7** observed and simulated time series of OH and HO_2 for the PRD case. The "Obs" subscript denotes the observation data. "Base" denotes the result of Baseline scenario as described on Box Model section. "Cons" denotes the results with additional constrained species compare to "Base". "$2.5 \times K_{HO2+NO}$" denotes the results with increasing the reaction rate coefficient of R11 by a factor of 2.5
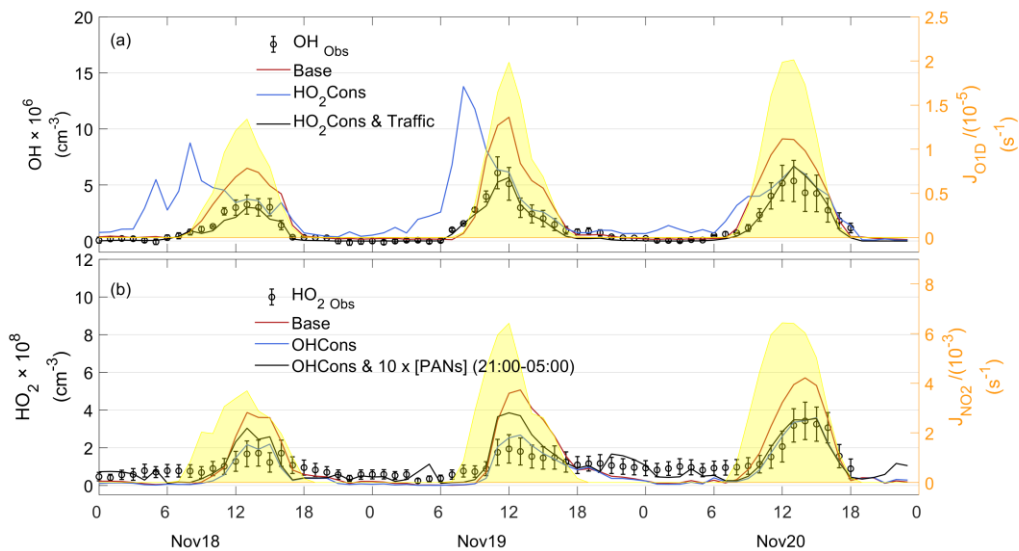
Figure 8 observed and simulated time series of OH and HO_2 for the CEC case. The "Obs" subscript denotes the observation data. "Base" denotes the result of Baseline scenario as described on Box Model section. "Cons" denotes the results with additional constrained species compare to "Base". "Traffic" denotes the sensitivity test results with consideration of vehicular emission (see Test S6 in SI). "$10 \times$ [PANs] (21:00-05:00)" denotes the results with increasing nighttime PANs concentration by a factor of 10.
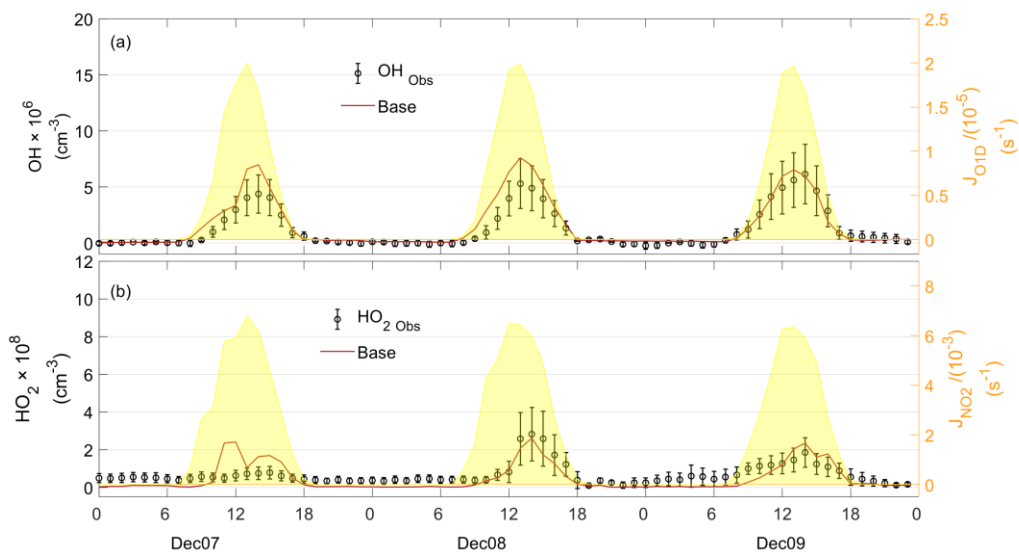

Figure 9 observed and simulated time series of OH and HO_2 for the CNC case. "Base" denotes the result of Baseline scenario as described on Box Model section.

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 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 remain 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).

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."
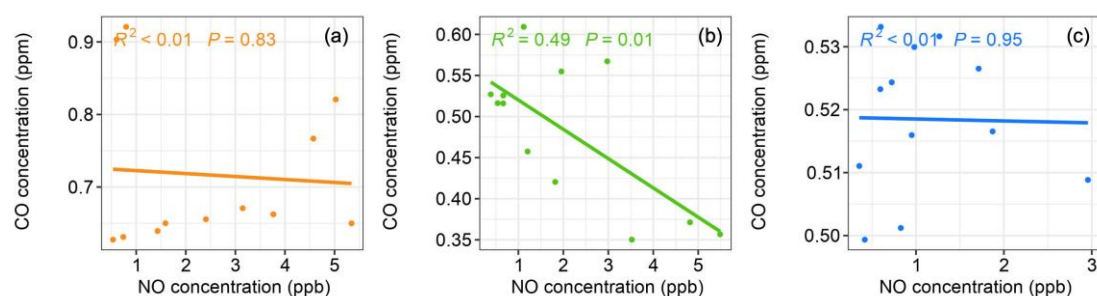
Additional Figure in SI:

Figure S6 Relationship between NO and CO concentrations in (a) PRD, (b) CEC and (c) CNC from 7:00 to 10:00. The solid lines depict the linear regression fit, with the corresponding equations R^2 and P values annotated on the plot.

Revised Text S7 on 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.

Q9: *The number of significant figures reported for parameters should align with the detection limits of the instrument. Retaining two decimal places for all parameters, irrespective of their precision, is inconsistent.*

Response: We have adjusted all values aligning with the instrument's detection limits.

Q10: *The units in Figure 5 should be corrected from 'ppb/s' to 'ppb/h' for consistency and to align with the typical units used in radical budget analysis.*

Response: We have updated the units in Figure 6 (Figure 5 in previous version) from 'ppb/s' to 'ppb h^{-1}'.

Q11: *In the legend of Figure 5a, the reaction "OH + NO_2" should be correctly identified as forming HNO_3 rather than HO_2.*

Response: Thank you for pointing this out. We have revised the legend in Figure 5.

Q12: *The manuscript inconsistently classifies the measurement site. Although it is described as a rural site, Figure S5 attributes it to a forest environment. Furthermore, the observed BVOC concentrations are much lower than AVOC concentrations, indicating a rural rather than a forested environment. This ambiguity should be resolved for clarity.*

Response: We acknowledge the inconsistency in describing the measurement site. The revised manuscript will attribute the result to a rural site in Figure S5, and throughout the manuscript.

Q13: *The manuscript lacks an assessment of the model's performance in simulating key species such as ozone and OVOCs. Given the uncommon degree of HO_x overestimation in a similar environment, evaluating the model's performance against observed concentrations of these species is necessary to validate the findings.*

Response: Our box model is constrained with both observed VOCs and OVOCs to calculate OH, and HO_2. The box model is not suitable for predicting Ozone and OVOC concentrations due to the lack of regional transport process. Because of the limited number of OVOCs measured in our study, it is likely our model underestimate OVOCs contribution to HO_2, which would lead to larger over-prediction of HO_2.