Dear Editor Eleanor Browne and Referee,

Thanks for your suggestions which significantly help us to improve the manuscript. Hereby, we submit our responses and the manuscript has been revised accordingly. If there are any further questions or comments, please let us know.
Best regards

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Major Comments

1. The authors did not conduct any testing for potential interferences associated with their OH measurements. While it is clear that some LIF-FAGE instruments are more sensitive to interferences than others, testing for interferences is still important, especially in complex chemical environments given that the source(s) of the interference have yet to be identified. The authors should acknowledge the possibility that unknown interferences may have contributed to their OH measurements and may explain some of the discrepancy with their model. It is unfortunate that the authors did not conduct interference testing during the " *heavy* " *pollutionepisode. This would have provided confidence that the elevated OH concentrations during this period were free from interferences.*

Reply:

Thanks for your suggestion. During the TROPSTECT-YRD campaign, we did not use an inlet-pre-injector to determine the chemical background of OH radical. We acknowledge your point that the comparison exercise with a second LIF instrument at a different location does not ensure that the instrument (and the OH measurement presented here) is free from interferences. We will discuss whether internal interference exists in AIOFM-LIF from the following aspects:

First of all, literature research shows that measurement interference is more related to the length of the inlet in the low-pressure cell (Griffith et al., 2016). In terms of system design, the AIOFM-LIF system uses a short-length inlet design to minimize this and other unknown disturbances (the distance from radical sampling to flourescence excitation is \sim 150 mm).

Additionally, potential interference may exist when the atmosphere contains abundant alkenes, ozone, and BVOCs, indicating that environmental conditions play leading roles in OH interferences (Mao et al., 2010; Fuchs et al., 2016; Novelli et al., 2014). In the previous comparison exercise with a LIF instrument deployed an inlet pre-injector (PKU-LIF), the ozonolysis interference on the measurement consistency of both systems was excluded under high-VOCs conditions (Zhang et al., 2022).

We have compared the chemical conditions during the intercomparison experiment and the current environmental conditions. Overall, the key parameters related to ozonolysis reactions $(O_3,$ alkenes, isoprene and NOx) in TROPSTECT-YRD were similar to those during the comparison experiment, which is not conducive to generating potential OH interference.

Table. Comparison of key parameters related to ozonolysis reactions (O_3, Ω) alkenes, isoprene and NOx) between TROPSTECT-YRD and the intercomparison experiment. All the values are the diurnal average $(10.00 - 15.00)$

| $\frac{1}{2}$ | | |
|----------------|------------------------|----------------------|
| Species | Intercomparison | TROPSTECT-YRD |
| O_3 (ppb) | 71.02 | 76.25 |
| Alkenes (ppb) | 1.29 | 0.67 |
| Isoprene (ppb) | 0.67 | 0.86 |
| NOx (ppb) | 5.65 | 6.55 |

To provide direct evidence on the OH chemical background signal, we conducted another atmospheric oxidation observation in the same location (Science Island background station in Hefei) and season (September, Autumn in 2022) in 2022, using chemical modulation methods to measure the chemical background of OH radicals in AIOFM-LIF instrument. The environmental conditions during ozone pollution (2022.9.29-2022.10.3) are shown in the Fig. S3, with daytime peaks of ozone concentration above 75 ppb, accompanied by alkene species approaching ~ 10 ppb. The diurnal concentration of isoprene was also a high level (>1 ppb). The chemical conditions are more favourable to induce OH interference than the TROPSTECT-YRD site. However, the OH concentrations achieved by chemical modulation (OH_{chem}) and wavelength modulation (OH_{way}) were in good agreement. No obvious chemical background was observed by deploying an inlet pre-injector. Therefore, it is not expected that OH measurement in the present study was affected by internal interference.

Fig. S3. Results of an additional atmospheric oxidation observation experiment in the same location and season in 2022. **(a)** Ozone concentration **(b)** Concentrations ofalkene and isoprene, respectively. **(c)** The OH concentrations achieved by chemical modulation (OH_{chem}) and wavelength modulation (OH_{wav}).

We added the detailed description in Line 187-197.

Revision:

Line 187-197: An additional atmospheric oxidation observation was conducted in the same location and season in 2022 with a chemical modulation method to determine the chemical background of OH radicals (Fig. S3). During the ozone pollution (2022.9.29-2022.10.3), the daytime peaks of ozone concentration above 75 ppb, accompanied by alkene species approaching \sim 10 ppb. The diurnal concentration of isoprene was also a high level $(>1$ ppb). The chemical conditions are more favourable to induce OH interference than in the TROPSTECT campaign, while the OH concentrations achieved by chemical modulation (OH_{chem}) and wavelength modulation (OH_{wav}) were in good agreement. No obvious chemical background was observed by deploying an inlet pre-injector. Therefore, it is not expected that OH measurement in the present study was affected by internal interference.

2. There is very little discussion of the OH reactivity measurements. Figure 4 shows the measured reactivity with that calculated from major OH sinks, but it *isn*'*t clear whether these are the measured OH sinks or whether they include the reactivity of unmeasured modeled oxidation products. During the* "*heavy*" *pollution episode, the calculated reactivity appears to be higher than that during the* "*semi*" *periods, while the measured reactivity appears to be similar. Given that the greatest discrepancy between the radical measurements and the model occurred during the*"*heavy*"*episode, the modeled OH reactivity (including the reactivity of unmeasured modeled oxidation products) should be discussed in much more detail.*

Reply:

Thanks for your suggestion. First, we provided a detailed description of the k_{OH} measurement instruments and listed the VOCs involved in the model simulations in Table S3.

Accordingly, we detailed the contribution of OVOCs to OH reactivity and analyzed the reasons for the differences between calculated and observed values (Fig.4). In Fig. 4, k_{OVOCs} are categorized into three groups: $k_{\text{OVOCs(Obs)}}$, $k_{\text{OVOCs(Model)}}$,

and *k*_{HCHO}. Given the significance of formaldehyde photolysis, the contribution of HCHO to k_{OVOCs} is distinguished. $k_{\text{OVOCs(Obs)}}$ encompasses species observed in addition to formaldehyde, such as acetaldehyde (ACD) and the oxidation products of isoprene (MACR and MVK). Intermediates generated by the model, including glyoxal (GLY), methylglyoxal (MGLY), higher aldehydes (ALD), ketones (KET), methyl ethyl ketone (MEK), and methanol (MOH), are classified as $k_{\text{OVOCs(Model)}}$. Upon considering $k_{\text{OVOCs(Mode)}}$, the calculated reactivity seems to compare well with the observed OH reactivity at the start of the measurement period, but then there is evidence of missing OH reactivity after September 10th (Fig.4(d)).

Fig. 4. Timeseries of the observed and modelled parameters for OH, HO₂ and k_{OH} during the observation period. **(a)** OH, **(b)** HO2, **(c)** *k*OH.

Due to the limitations of available instruments, this observation only measured a limited number of OVOCs species, making it difficult to accurately quantify the contribution of larger aldehydes and ketones, carboxylic acids, nitrophenols, and other multifunctional species to k_{OH} (Wang et al., 2024). Since the MCM mechanism considers more secondary formation reactions than the RACM2 mechanism, it can qualitatively assess the photochemical role of unmeasured OVOCs species in the atmosphere (Wang et al., 2022). The additional modeled OVOCs by the MCM v3.3.1

mechanism contributed \sim 2.4 s⁻¹ to the missing OH reactivity (Fig.S6). During Heavy period, the reactivity of more model oxidation products increased the daytime k_{OH} by about 5.1 s⁻¹. Therefore, the observed k_{OH} can serve as an upper limit for sensitivity tests, thereby the full suite of radical measurement can be performed to explore the missing oxidation properties and ozone formation (Section 4.1).

Fig. S7. Timeseries of the observed and modelled k_{OH} during the observation period.

We added the detailed description in Line 345-353&372-386. **Revision:**

Line 345-353: k_{OVOCs} are categorized into three groups: $k_{\text{OVOCs(Obs)}}$, $k_{\text{OVOCs(Model)}}$, and *k*HCHO. Given the significance of formaldehyde photolysis, the contribution of HCHO to *k*OVOCs is distinguished. *k*OVOCs(Obs) encompasses species observed in addition to formaldehyde, such as acetaldehyde (ACD) and the oxidation products of isoprene (MACR and MVK). Intermediates generated by the model, including glyoxal (GLY), methylglyoxal (MGLY), higher aldehydes (ALD), ketones (KET), methyl ethyl ketone (MEK), and methanol (MOH), are classified as $k_{\text{OVOCs(Model)}}$. Upon considering *k*OVOCs(Model), the reactivity calculated prior to September 10th aligns quite well with the observed OH reactivity.

Line 372-386: The calculated reactivity seems to compare well with the observed OH reactivity at the start of the measurement period, but then there is evidence of missing OH reactivity after September 10th (Fig. $4(d)$). Due to the limitations of available instruments, this observation only measured a limited number of OVOCs species, making it difficult to accurately quantify the contribution of larger aldehydes and ketones, carboxylic acids, nitrophenols, and other multifunctional species to k_{OH} (Wang et al., 2024). Since the MCM mechanism considers more secondary formation reactions than the RACM2 mechanism, it can qualitatively assess the photochemical role of unmeasured OVOCs species in the atmosphere (Wang et al., 2022). The additional modeled OVOCs by the MCM v3.3.1 mechanism contributed \sim 2.4 s⁻¹ to to the missing OH reactivity(Fig. S7). During Heavy period, the reactivity of more model oxidation products increased the daytime k_{OH} by about 5.1 s⁻¹. Therefore, the observed k_{OH} can serve as an upper limit for sensitivity tests, thereby the full suite of radical measurement can be performed to explore the missing oxidation properties and ozone formation (Section 4.1).

3. As noted in the manuscript, there have been several studies where the " *X mechanism*" *has been incorporated in order to explain the underprediction of the measured OH concentration by the model (Table 1). However, similar to these previous studies, the authors do not provide any new insight on what* "*X*" *might be. Some of these authors have recently published a theoretical study suggesting that reactive aldehyde chemistry may explain the missing source of OH (Yang et al.,Nature Communications, 15, 1648 (2024). https://doi.org/10.1038/s41467-024-45885-w). Incorporation of this proposed mechanism into their model would provide some new insights into the potential missing radical chemistry and provide a test of whether the proposed mechanism can explain the measured radical concentrations during the heavy pollution episode.*

Reply:

Thank you for your review and valuable comments on this manuscript. We agree with your perspective on species X, considering that it currently serves more as a fitting parameter, which may offer limited assistance in understanding the underlying mechanisms. Therefore, in this revision, we have followed your advice and added the Higher Aldehyde Mechanism to test whether it can explain the discrepancy between measured and simulated radical concentrations. The results indicate that the contribution of the HAM mechanism to OH radicals in different episodes ranged between 4.4% - 6.0%, while the concentrations of $HO₂$ and $RO₂$ radicals increased by approximately 7.4% and 12.5%, respectively.

Fig. 7. The response of **(a)** OH, **(b)** HO² and **(c)** RO² radicals to the Higher Aldehyde Mechanism (HAM) in different episodes (Semi I, Heavy, and Semi II) in diurnal time (10:00-15:00).

Additionally, we combine the missing aldehyde primary emissions and the HAM mechanism under the entire photochemical spectrum to qualitatively assess the impact on $RO₂$ radical concentrations. Notably, $RO₂$ radical concentrations exhibit a pronounced sensitivity to autoxidation, with the incorporation of additional OVOCs potentially boosting simulated RO² radical concentrations by 20% to 40%. Consequently, although limiting formaldehyde can partially offset the $HO₂$ radical cycle and enhance the precision of HOx radical chemistry studies, additional measurements should be undertaken for other OVOCs, coupled with the deployment of full-chain radical detection systems, to accurately elucidate the oxidation processes under severe ozone pollution conditions.

Fig. S12. The relationship between the differences in the simulation of **(a)** OH, **(b)** HO2, and (c) RO₂ radical concentrations by HAM mechanism and the base scenario across the entire photochemical spectrum. An empirical hypothesis is proposed to amplify the concentration of higher-order aldehydes by a factor of about 4, which is the proportion of formaldehyde concentration underestimated by the model. The boxplots represent the 10%, 25%, median, 75%, and 90% of the data, respectively.

Revision:

Line 508-518: Missing OH sources are closely related to the chemistry of OVOCs(Yang et al., 2024a; Qu et al., 2021). Reactive aldehyde chemistry, particularly the autoxidation of carbonyl organic peroxy radicals $(R(CO)O₂)$ derived from higher aldehydes, is a significant OH regeneration mechanism that has been shown to contribute importantly to OH sources in regions with abundant natural and anthropogenic emissions during warm seasons(Yang et al., 2024b). In this study, the higher aldehyde mechanism (HAM) by Yang et al was parameterized into the base model to test new insights into the potential missing radical chemistry (Fig. 7). The results indicate that the contribution of the HAM mechanism to OH radicals in different episodes ranged between 4.4% - 6.0% , while the concentrations of HO₂ and RO² radicals increased by approximately 7.4% and 12.5%, respectively.

Line 556-569: Higher aldehyde chemistry is a concrete manifestation of verifying the aforementioned hypothesis for $RO₂$ sources(Yang et al., 2024b). The autoxidation process of R(CO)O2, encompasses a hydrogen migration process that transforms it into the ·OOR(CO)OOH radical(Wang et al., 2019). This radical subsequently reacts with NO to yield the ·OR(CO)OOH radical. The ·OR(CO)OOH radical predominantly undergoes two successive rapid hydrogen migration reactionss, ultimately resulting in the formation of $HO₂$ radicals and hydroperoxy carbonyl (HPC). Consequently, the HAM mechanism extends the lifetime of the $RO₂$ radical, providing a valuable complement to the unaccounted sources of $RO₂$ radicals. As depicted in Fig. 7, the incorporation of the HAM mechanism results in an approximate 7.4% and 12.5% increase in the concentrations of $HO₂$ and $RO₂$ radicals, respectively. It is important to note that the total concentrations of primary emitted aldehydes and the HPC group may be underestimated, which could lead to the aforementioned analysis being conservative in nature. Further exploration of the unaccounted sources of $RO₂$ radicals will be presented in Section 4.3.

Line 682-712: The reasons for the discrepancy between simulated and observed values for ozone production deserve further investigation. As depicted in Fig.11(c), the simulated HO₂/RO₂ ratios display a robust positive correlation with photochemical activity, fluctuating between 2 and 4. A notable feature during severe ozone pollution is the intense distribution of formaldehyde, with an average concentration of 21.81 \pm 4.57 ppb (11:00 – 13:00). While formaldehyde acts as a precursor for HO_2 radicals, it does not directly generate RO₂ radicals. The contributions of OVOCs to the RO_x radical do not exhibit the same intensity as formaldehyde, and the current mechanism encounters difficulties in replicating formaldehyde concentrations (Fig. S11). The simulation of formaldehyde concentrations using the MCM v3.3.1 mechanism has shown improvement, indicating that the secondary formation of unmeasured species, such as OVOCs, will feedback on RO₂ radical levels. When formaldehyde levels are unconstrained, the simulated HO_2/RO_2 ratios align with observations, suggesting that under the prevailing chemical mechanism, the photochemical efficiency of formaldehyde and other OVOCs is similar. Therefore, an empirical hypothesis is proposed to amplify the concentration of higher-order aldehydes by a factor of about 4, which is the proportion of formaldehyde concentration underestimated by the model.

The qualitative assessment of the impact of missing aldehyde primary emissions on RO² radical concentrations was combined with the HAM mechanism across the entire photochemical spectrum (Fig.S12). Enhanced impact of aldehyde autoxidation in the presence of weak photochemical conditions could alter the simulated levels of OH and HO² radicals by approximately 13.9% and 18.1%, respectively. However, higher ALD concentrations will be achieved under intensive photochemical conditions, leading to the gradual dominance of the sink channels for $OH + OVOCs$, with the effect of autoxidation mechanisms gradually decreasing. RO₂ radical concentrations is notably more sensitive to the HAM mechanism, where incorporates additional OVOCs, can enhance the simulation of $RO₂$ radical concentrations by 20 - 40%.
Consequently, although limiting formaldehyde can partially offset the HO₂ radical cycle and enhance the precision of HOx radical chemistry studies, additional measurements should be undertaken for other OVOCs, coupled with the deployment of full-chain radical detection systems, to accurately elucidate the oxidation processes under severe ozone pollution conditions.

4. The final section of the paper is very confusing. The authors appear to suggest that the base model constrained to the measured formaldehyde overestimates the HO2/RO2 ratio by increasing the production of HO2 relative to RO2. However, unconstraining the model to the formaldehyde concentrations results in lower HO2/RO2 ratios that are in better agreement with the measured ratio, presumably because the model underestimates the measured formaldehyde. However, including monoterpene chemistry that have multiple RO2 isomerization steps increases the modeled RO2 concentration so that the modeled HO2/RO2 ratio is in better agreement with the measurements when HCHO is constrained. The authors suggest that additional measurements of OVOCs are necessary, but the connection between unmeasured OVOCs and the dif erent model scenarios discussed in this section is not clear. This section of the manuscript needs considerable revision in order to clarify the points that the

authors are trying to make.

Reply:

Thank you for your response. We acknowledge your point that the final section of the paper is very confusing.We wish to elaborate on a phenomenon in the manuscript, which is that formaldehyde has a high concentration distribution (average noon concentration of 21.81 ± 4.57 ppb), but OVOCs do not show the same intensity in contributing to ROx radicals as formaldehyde does. The current mechanism is having difficulty replicating the concentration of formaldehyde. Therefore, we have changed the title of the relevant section to "4.3 Missing OVOCs sources influence ozone production" and adjusted the content of that section. We have removed the impact of formaldehyde on the length of the reaction chain and its oxidizing effect, focusing more on the diagnostic of the HO_2/RO_2 ratio on ozone formation to improve the readability of the manuscript.

We also analyzed the impact of the missing OVOCs sources on RO₂ radicals and ozone production. When formaldehyde levels are unconstrained, the simulated HO2/RO² ratios align with observations, suggesting that under the prevailing chemical mechanism, the photochemical efficiency of formaldehyde and other OVOCs is similar. Therefore, an empirical hypothesis is proposed to amplify the concentration of higher-order aldehydes by afactor of about 4, which is the proportion of formaldehyde concentration underestimated by the model. The qualitative assessment of the impact of missing aldehyde primary emissions on $RO₂$ radical concentrations was combined with the HAM mechanism across the entire photochemical spectrum (Fig.S12). Enhanced impact of aldehyde autoxidation in the presence of weak photochemical conditions could alter the simulated levels of OH and $HO₂$ radicals by approximately 13.9% and 18.1%, respectively. However, higher ALD concentrations will be achieved under intensive photochemical conditions, leading to the gradual dominance of the sink channels for $OH + OVOCs$, with the effect of autoxidation mechanisms gradually decreasing. $RO₂$ radical concentrations is notably more sensitive to the HAM mechanism, where incorporates additional OVOCs, can enhance the simulation of $RO₂$ radical concentrations by 20 - 40%.

We added the detailed description in Line 661-712.

Fig. S12. The relationship between the differences in the simulation of **(a)** OH, **(b)** HO2, and **(c)** RO² radical concentrations by HAM mechanism and the base scenario across the entire photochemical spectrum. An empirical hypothesis is proposed to amplify the concentration of higher-order aldehydes by a factor of about 4, which is the proportion of formaldehyde concentration underestimated by the model. The boxplots represent the 10%, 25%, median, 75%, and 90% of the data, respectively.

Revision:

Line 660: 4.3 Missing OVOCs sources influence ozone production

Line 661-712: The consistency between model predictions and observed measurements for ozone production, akin to the concentration ratio of HO_2/RO_2 , is depicted in Fig. 11(a)(b). In areas with low NO levels, the ratio of modeled to actual ozone production ranges from 0.5 to 2, with the exception of the ClearfLo and AIRPRO-summer datasets(Woodward-Massey et al., 2023; Whalley et al., 2021). Conversely, under high NO conditions (with NO concentrations between 3 and 6 ppbv), the ozone production rate $(P(Ox))$ derived from measured radical concentrations typically exceeds that of the base model's predictions by more than threefold. Laboratory experiments focusing on the oxidation of representative VOCs suggest that ozone production can be enhanced by approximately 25% for the anthropogenic VOCs under investigation(Färber etal., 2024). The MTS+X scenario represents an effort to enhance the congruence between modeled and measured radical concentrations. The incorporation of OVOCs and larger alkoxy radicals derived from monoterpenes has refined the model-measurement agreement for ozone formation under high NO conditions, reducing the discrepancy from 4.17 to 2.33. This substantiates the hypothesis of sensitivity analysis concerning ozone generation, as detailed in Section 4.2 and illustrated in Fig. S10.

Fig. 11. Summary of the $P(Ox)_{Obs}/P(Ox)_{Mod}$ under (a) low-NO and (b) high-NO conditions.(c) The ratios for HO2/RO² show a correlation with HCHO levels. The blue shading represents the range of variation from constrained to unconstrained formaldehyde conditions. Charmber Exp. 1 and Charmber Exp. 2 denotes the parameters by single-step HO₂ formation and multi-step HO₂ formation determined in the chamber by (Färber et al., 2024).

The reasons for the discrepancy between simulated and observed values for ozone production deserve further investigation. As depicted in Fig.11(c), the simulated HO_2/RO_2 ratios display a robust positive correlation with photochemical activity, fluctuating between 2 and 4. A notable feature during severe ozone pollution is the intense distribution of formaldehyde, with an average concentration of 21.81 \pm 4.57 ppb (11:00 – 13:00). While formaldehyde acts as a precursor for HO_2 radicals, it does not directly generate RO² radicals. The contributions of OVOCs to the ROx radical do not exhibit the same intensity as formaldehyde, and the current mechanism encounters difficulties in replicating formaldehyde concentrations (Fig. S11). The simulation of formaldehyde concentrations using the MCM v3.3.1 mechanism has shown improvement, indicating that the secondary formation of unmeasured species, such as OVOCs, will feedback on $RO₂$ radical levels. When formaldehyde levels are unconstrained, the simulated $HO₂/RO₂$ ratios align with observations, suggesting that

under the prevailing chemical mechanism, the photochemical efficiency of formaldehyde and other OVOCs is similar. Therefore, an empirical hypothesis is proposed to amplify the concentration of higher-order aldehydes by a factor of about 4, which is the proportion of formaldehyde concentration underestimated by the model. The qualitative assessment of the impact of missing aldehyde primary emissions on RO² radical concentrations was combined with the HAM mechanism across the entire photochemical spectrum (Fig.S12). Enhanced impact of aldehyde autoxidation in the presence of weak photochemical conditions could alter the simulated levels of OH and HO² radicals by approximately 13.9% and 18.1%, respectively. However, higher ALD concentrations will be achieved under intensive photochemical conditions, leading to the gradual dominance of the sink channels for $OH + OVOCs$, with the effect of autoxidation mechanisms gradually decreasing. RO₂ radical concentrations is notably more sensitive to the HAM mechanism, where incorporates additional OVOCs, can enhance the simulation of $RO₂$ radical concentrations by 20 - 40%.
Consequently, although limiting formaldehyde can partially offset the HO₂ radical cycle and enhance the precision of HOx radical chemistry studies, additional measurements should be undertaken for other OVOCs, coupled with the deployment of full-chain radical detection systems, to accurately elucidate the oxidation processes under severe ozone pollution conditions.

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