Response to Reviewer comment #1:

General comments:

The authors have done a lot of work to improve the paper. My main concerns were on the quality of the data set, because in my opinion some major data were missing:

Reply

We gratefully thank you for all the suggestions which are helpful for the important guiding significance to us. Below are our responses to the specific comments, highlighted in blue, with changes to the manuscript highlighted in green.

Specific comments:

1. Total OH reactivity: in the revised version, such measurements have appeared for a short period during the campaign. These data show a good agreement with the model, so I am really wondering why these data have not been shown in the original version of the manuscript. Anyway, these data allow now to get a better confidence in the data treatment concerning the OH losses.

Reply

Thanks for your affirmation about the OH reactivity in the original comments.

2. HO_2 measurements where done at very high NO concentrations for HO_2 conversion in order to use the HO_2 signal as reference cell for stabilizing the laser wavelength. In the revised version, the calibration of HO_2 with increasing added NO concentration has been discussed, and indeed under the "low" NO conditions the HO_2 conversion rate is up to 95%, while under the "high" NO conditions the conversion rate is over 100%, showing that RO_2 interference plays a role in both conditions. However, no RO_2 measurements are available from this campaign, and therefore the correction of the HO_2^* signal can only be done based on modelled RO_2 concentrations and supposed RO_2 interference yields. It is not really clear to me, which RO_2 interference yields have been used for correction: did the authors measure it themselves or did they use data from Fuchs et al? This increases the uncertainty on the HO_2 concentration, and thus on the OH data as well.

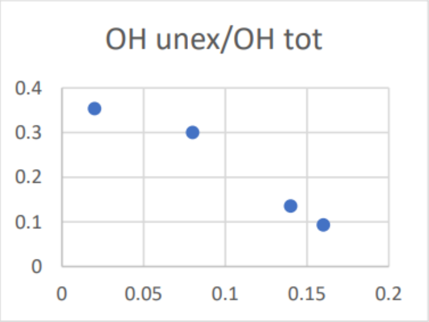
Reply

The RO_2 interference yields which have been used for correction were the reported data in Lu et al. (2012). Herein, the RO_2 species include methane, ethane, propane, n-butane, i-pentane, n-hexane, n-heptane, 2-methylhexane, 3-methylhexane, cyclohexane, ethene, propene, 1-butene, 1-pentene, cis-2-butene, trans-2-butene, trans-2-pentene, isoprene, MACR, MVK, benzene, toluene, ethylbenzene, o-xylene, m-xylene, p-xylene, styrene, and 1,2,4-trimethylbenzene (Lu et al., 2012). Lu et al. (2012) reported the experimental values and the modeled values simultaneously, and we used the modeled values by MCMv3.2 here. Herein, we further added the description of the RO_2 interference yields in Section 2.2 in the revised manuscript.

Revision

The RO_2 interference yields which was used for correction were the modeled values reported by Lu et al. (2012).

3. The OH concentration is underestimated by the model at low NO concentrations, and this disagreement has even increased since the HO_2 concentration has been corrected for RO_2 interference. The mysterious X species has been added to the model, and its concentration has been adjusted to bring into better agreement model and measurement. There is now some discussion on the concentration of this species and comparison with earlier studies. However, I am still regretting that the pre-injector system has not been used in this campaign to fully exclude any interference in the OH measurements. The argument that the PKU-LIF instrument has been proven free from interference in earlier campaigns, thus demonstrating the accuracy of the PKU-LIF system, does not fully convince me neither: looking for example to the Wangdu data, where a pre-injector has been used, some unexplained OH has been detected. There is a table in the paper giving the unexplained OH concentration together with NO and total OH concentrations. If one plots this unexplained OH (divided by total OH in order to normalize to overall photochemical activity) as a function of NO concentration, one gets a clear increase of the unexplained OH with decreasing NO:



In the new version, the authors at least mention that there have been reports on interferences in OH measurements when sampled air contains ozone, alkenes and BVOCs. They do not mention that also an interference has been detected in FAGE instruments due to ROOOH, the product of the reaction of RO_2 with OH (Atmos. Chem. Phys. 2019, 19, 349-362). In a very recent Science paper by Berndt et al. (Hydrotrioxide (ROOOH) formation in the atmosphere. Science 2022, 376, 979-982) it is experimentally proven that ROOOH species have lifetimes of up to several hours, and that in low NO environments up to 1% of isoprene can be transformed to various ROOOH species. Even if RO_2 concentrations have not been measured during this campaign, the reaction of RO_2 + OH should be added to the mechanism and the sum of modelled ROOOH concentrations should be compared against the modelled underestimation of OH concentration.

Reply

Thanks for your helpful suggestions. The data presented in the above figure were from 13:00-15:00 on 29 June, 14:40-16:10 on 30 June, 16:30-17:40 on 05 July, and 18:00-21:00 on 05 July in Wangdu campaign (Tan et al., 2017). The isoprene and O_3 concentrations varied within 1.4-2.8 ppb and 77-126 ppb, respectively. Herein, to compare the environmental conditions between Wangdu campaign and Shenzhen campaign, we presented the mean O_3 and isoprene concentrations in Shenzhen campaign during the corresponding period in Wangdu campaign (13:00-15:00, 14:40-16:10, 16:30-17:40 and 18:00-21:00) in the below table. The mean isoprene concentrations were 0.1-1.2 ppb, 0.1-0.7 ppb, 0.1-1.2 ppb, and 0.1-1.1 ppb in the four periods, which were all lower than the corresponding periods of Wangdu campaign. In terms of the O_3 concentrations, the mean O_3 concentrations were 11-109 ppb, 13-119 ppb, 8-116 ppb and 3-71 ppb in the four periods. The O_3 concentrations in Shenzhen during the 13:00-15:00 period and the 18:00-21:00 period were all lower than those during the corresponding periods in Wangdu. As for the O_3 concentration during the 14:40-16:10 period and the 16:30-17:40 period, only the O_3 concentration on 07-08 October were higher than those during the corresponding periods in Wangdu, but the isoprene concentrations on 07-08 October in Shenzhen were significantly lower than those in Wangdu. Overall, Tan et al. (2017) reported that the unknown OH interference have a minor impact on the daytime OH measurements. Thus, we can believe that the OH interference have a minor impact on the daytime OH observations from the perspective of the environmental conditions in this study by comparing the isoprene and O_3 concentrations in Shenzhen and Wangdu.

Table: The mean O_3 and isoprene concentrations in Shenzhen campaign during the corresponding period of Wangdu campaign (13:00-15:00, 14:40-16:10, 16:30-17:40 and 18:00-21:00).

Date / Species	10-05	10-06	10-07	10-08	10-09	10-10	10-11	10-12	10-13	10-14	10-15	10-16
O_3 (ppb) 13:00-15:00	86	98	109	109	63	32	34	54	62	43	43	25
O_3 (ppb) 14:40-16:10	82	98	98	119	70	32	36	48	61	41	43	18
O_3 (ppb) 16:30-17:40	83	94	116	81	49	22	38	37	46	40	36	8
O_3 (ppb) 18:00-21:00	42	57	71	61	27	22	27	15	38	37	30	11
Isoprene (ppb) 13:00-15:00	0.4	0.4	0.6	0.4	0.5	0.4	0.1	0.4	0.5	0.5	0.4	0.3
Isoprene (ppb) 14:40-16:10	0.6	0.4	0.5	0.4	0.4	0.3	0.2	0.2	0.3	0.3	0.4	0.2
Isoprene (ppb) 16:30-17:40	1.2	0.2	0.2	0.2	0.3	0.2	0.1	0.1	0.3	0.2	0.2	0.1
Isoprene (ppb) 18:00-21:00	1.1	0.1	0.1	0.1	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.1

Date / Species	10-17	10-18	10-19	10-20	10-21	10-22	10-23	10-24	10-25	10-26	10-27	10-28
O_3 (ppb) 13:00-15:00	11	25	50	54	54	15	62	48	60	95	77	78
O_3 (ppb) 14:40-16:10	13	27	42	54	51	19	65	49	62	74	77	72

O_3 (ppb) 16:30-17:40	13	26	47	46	38	14	47	45	51	56	70	63
O_3 (ppb) 18:00-21:00	3	14	37	33	41	2	29	33	28	20	44	24
Isoprene (ppb) 13:00-15:00	0.1	0.2	0.6	0.3	1.4	0.8	0.5	0.4	0.5	1.1	0.8	1.2
Isoprene (ppb) 14:40-16:10	0.1	0.1	0.3	0.2	0.8	0.6	0.7	0.2	0.3	0.7	0.6	0.7
Isoprene (ppb) 16:30-17:40	0.1	0.1	0.1	0.1	0.5	0.3	0.3	0.2	0.2	0.5	0.5	0.6
Isoprene (ppb) 18:00-21:00	0.1	0.1	0.1	0.1	0.1	0.3	0.1	0.1	0.1	0.1	0.2	0.2

Besides the environmental conditions, the prior studies reported that the product of the reactions of RO_2 with OH, trioxides (ROOOH), might lead to an OH interference signal. The reactions of RO_2 radicals with OH radicals might be competitive with other sinks for RO_2 radicals (Fittschen, 2019;Fittschen et al., 2019;Berndt et al., 2022). However, Fittschen et al. (2019) reported that the ROOOH interference is highly dependent on the design and measurement conditions of different FAGE instruments. Therefore, we integrated the reactions of the ROOOH production and destruction into the base model herein, as shown in Eq. (1-2).

$$RO_2 + OH \rightarrow ROOOH \quad (1)$$

$$ROOOH \rightarrow RO + HO_2 \quad (2)$$

where the RO_2 is across all RO_2 radicals in the model excluding methyl peroxy radicals, for which it has been shown that the production of a trioxide species is only a minor product channel while the trioxide yield is expected to be close to 1 for larger peroxy radicals. The rate constant of Eq. (1) is 1.5×10^{-10} cm^3 s^{-1} (Fittschen et al., 2019). In Eq. (2), the rate constant is 10^{-4} s^{-1}, leading to ROOOH lifetimes of around 3 h, of the same order as the lifetime of ROOH species (Fittschen et al., 2019).

Figure. S1 (a) presents the modeled ROOOH concentrations during this campaign, and the maximum ROOOH concentration was 4.4×10^{9} cm^{-3}. The correlation of the modeled ROOOH concentrations and the ratios of OH observations to OH simulations, and the correlation of the modeled ROOOH concentrations and the difference between OH observations and simulations both demonstrated that no significant relevance between ROOOH and the underestimation of OH radicals, as shown in Fig. S1 (b-c). Additionally, the ROOOH values modeled in our another campaign (Taizhou, 2018) were comparable to or even slightly higher than the simulations in this study, and the chemical modulation tests in Taizhou confirmed the ROOOH is not a significant OH interference in our PKU-LIF system (Ma et al., 2022).

We have added the ROOOH interference in Section 2.2 in the revised manuscript and the revised Supplementary Information.

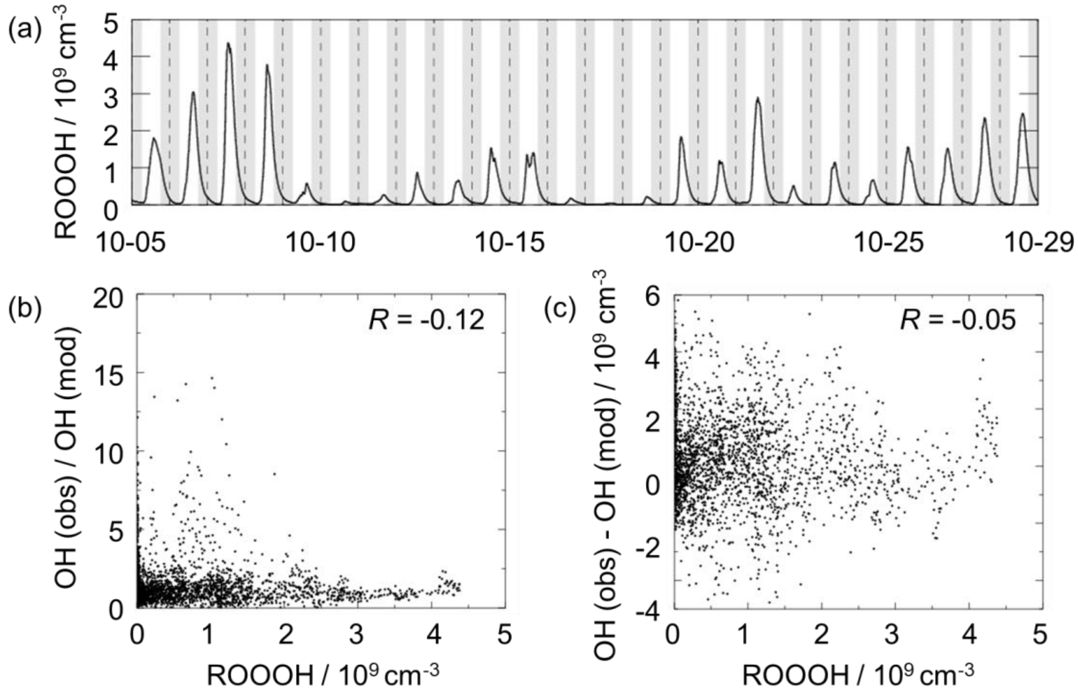


Figure S1: (a) The timeseries of ROOOH concentration from the reactions of RO_2 radicals excluding methyl peroxy radicals with OH radicals. (b) The correlation of the modeled ROOOH concentrations and the ratios of OH observations to OH simulations. (c) The correlation of the modeled ROOOH concentrations and the difference between OH observations and simulations. Only daytime values were chosen in (b-c).

Revision

(1) Section 2.2

Besides the environmental conditions, the prior studies reported that the product of the reaction of RO_2 with OH, trioxides (ROOOH), might lead to an OH interference signal. The reactions of RO_2 radicals with OH radicals might be competitive with other sinks for RO_2 radicals (Fittschen, 2019;Fittschen et al., 2019;Berndt et al., 2022). However, Fittschen et al. (2019) reported that the ROOOH interference is highly dependent on the design and measurement conditions of different FAGE instruments. Therefore, we integrated the reactions of the ROOOH production and destruction into the base model herein, with the ROOOH production rate constant of 1.5×10^{-10} cm^3 s^{-1} and the destruction rate constant of 10^{-4} s^{-1} (the details are presented in the Supplementary Information) (Fittschen et al., 2019). Figure. S1 (a) presents the modeled ROOOH concentrations during this campaign, with a maximum of about 4.4×10^9 cm^{-3}. The correlation of the modeled ROOOH concentrations and the ratios of OH observations to OH simulations, and the correlation of the modeled ROOOH concentrations and the difference between OH observations and simulations both demonstrated that no significant relevance between ROOOH and the underestimation of OH radicals, as shown in Fig. S1 (b-c). Additionally, the ROOOH values modeled in our another campaign (Taizhou, 2018) were comparable to or even slightly higher than the simulations in this study, and the chemical modulation tests in Taizhou confirmed the ROOOH is not a significant OH interference in our PKU-LIF system (Ma et al., 2022).

Overall, the OH interference during this campaign was negligible according to the analysis of the behavior of PKU-LIF system in previous campaigns, the comparison of environmental conditions between this campaign and Wangdu campaign, and the exploration of the impact of ROOOH on the discrepancy of OH observations and simulations. However, we should acknowledge that the unmeasured interference might have an effect on radical measurement. More precise chemical modulation tests are needed in the future.

(2) Figure S1 in the Supplementary Information

To evaluate the impact of the interference from ROOOH on radical concentrations, we integrated the reactions of the ROOOH production and destruction into the base model herein, as shown in Eq. (S1-S2).

$$RO_2 + OH \rightarrow ROOOH \qquad (S1)$$

$$ROOOH \rightarrow RO + HO_2 \qquad (S2)$$

where the RO_2 is across all RO_2 radicals in the model excluding methyl peroxy radicals, for which it has been shown that the production of a trioxide species is only a minor product channel while the trioxide yield is expected to be close to 1 for larger peroxy radicals. The rate constant of Eq. (S1) is 1.5×10^{-10} cm^3 s^{-1} (Fittschen et al., 2019). In Eq. (S2), the rate constant is 10^{-4} s^{-1}, leading to ROOOH lifetimes of around 3 h, of the same order as the lifetime of ROOH species (Fittschen et al., 2019).

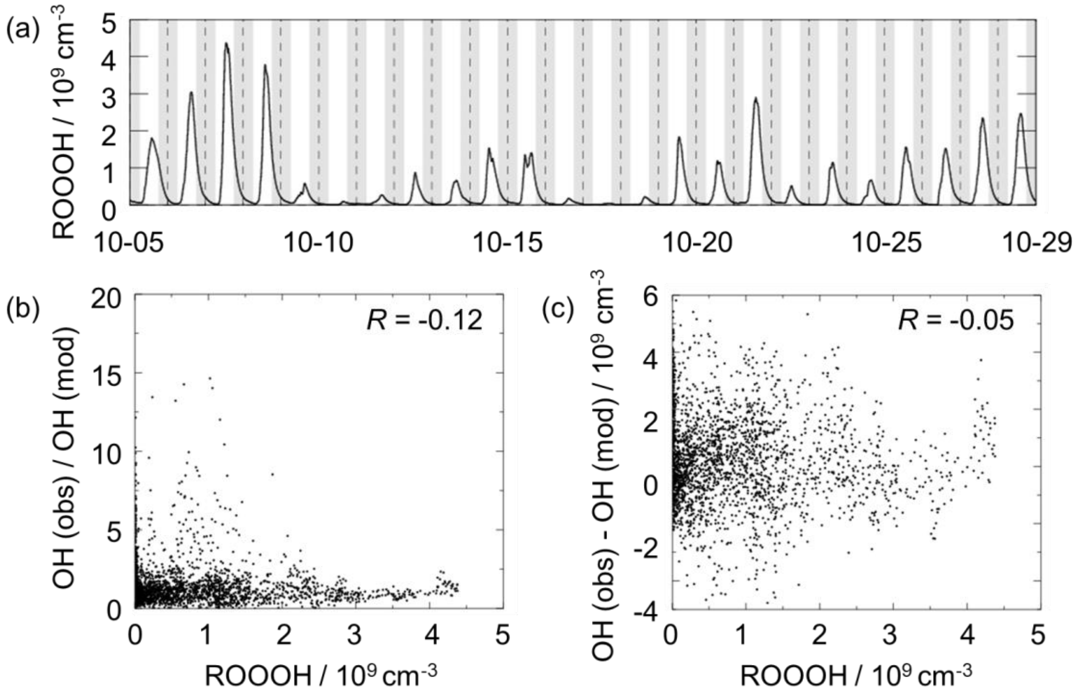


Figure S1: (a) The timeseries of ROOOH concentration from the reactions of RO_2 radicals excluding methyl peroxy radicals with OH radicals. (b) The correlation of the modeled ROOOH concentrations and the ratios of OH observations to OH simulations. (c) The correlation of the modeled ROOOH concentrations and the difference between OH observations and simulations. Only daytime values were chosen in (b-c).

References

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Fittschen, C.: The reaction of peroxy radicals with OH radicals, Chemical Physics Letters, 725, 102-108, 10.1016/j.cplett.2019.04.002, 2019.

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Ma, X. F., Tan, Z. F., Lu, K. D., Yang, X. P., Chen, X. R., Wang, H. C., Chen, S. Y., Fang, X., Li, S. L., Li, X., Liu, J. W., Liu, Y., Lou, S. R., Qiu, W. Y., Wang, H. L., Zeng, L. M., and Zhang, Y. H.: OH and HO2 radical chemistry at a suburban site during the EXPLORE-YRD campaign in 2018, Atmospheric Chemistry and Physics, 22, 7005-7028, 10.5194/acp-22-7005-2022, 2022.

Tan, Z., Fuchs, H., Lu, K., Hofzumahaus, A., Bohn, B., Broch, S., Dong, H., Gomm, S., Haeseler, R., He, L., Holland, F., Li, X., Liu, Y., Lu, S., Rohrer, F., Shao, M., Wang, B., Wang, M., Wu, Y., Zeng, L., Zhang, Y., Wahner, A., and Zhang, Y.: Radical chemistry at a rural site (Wangdu) in the North China Plain: observation and model calculations of OH, HO2 and RO2 radicals, Atmospheric Chemistry and Physics, 17, 663-690, 10.5194/acp-17-663-2017, 2017.

Response to Reviewer comment #2:

General comments:

The manuscript was improved upon revision. It is good to know that OH reactivity measurements were done at least partly during the field campaign and it gave a sense of accuracy of the analysis made in this study. However, more justification is needed particularly with the following points:

Reply

Thanks for your critical suggestions which would help us to improve the manuscript. We have studied all the comments which were helpful for revising and improving our manuscript. We have made corrections which we hope meet with approval. Below are our responses to the specific comments, highlighted in blue, with changes to the manuscript highlighted in green.

Specific comments:

1. Previous specific point #10:

   I would suggest an additional model sensitivity calculation where the constraint to the observation is removed and rather calculated for one of the measured OVOCs and see if the modeled levels agree with the observations. This will provide a sense if the turnover of the unmeasured OVOCs is well taken into account in the simulation.

Reply

Thanks for your suggestions, and we conducted the sensitivity calculation. Herein, we compared the observations and simulations of methyl vinyl ketone (MVK), which mainly derives from the oxidation of isoprene. The red lines denote the MVK observations, and the blue lines denote the MVK simulations when the constraint to the MVK observations is removed in the model. The comparison of the MVK observations and simulations indicated that the turnover of the unmeasured OVOCs is well taken into account in the simulations.

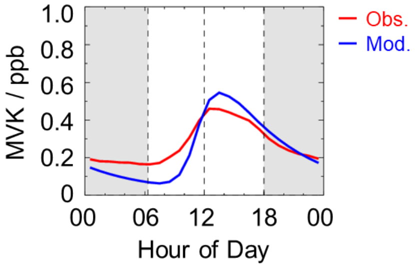

Figure: The diurnal profiles of methyl vinyl ketone (MVK) concentrations in this campaign.

2. Previous specific point #11:

   Discussion direction about the importance of heterogeneous reactions of HO_2 changed from the previous manuscript - from unimportant to important. Though the authors stated in their reply that "as the γ increased to approximately 0.3, good agreement between the modeled and observed HO_2＊ concentration was achieved, demonstrating that the significant heterogeneous uptake might exist in this campaign", their statements in the revised manuscript (L367, 536 in the Author's Tracked Changes (ATC) version) are very qualitative. The quantitative analysis included in the reply needs to be present in the manuscript.

Reply

Thanks for your helpful suggestions. We added a section (Section 4.3) to present the quantitative analysis in the revised manuscript.

Revision

(1) Section 4.3: HO_2 heterogeneous uptake

The HO_2 heterogeneous uptake has been proposed to be a potential sink of HO_2 radicals, and thus could influence the radical chemistry and the formation of secondary pollution, especially in high-aerosol environments (Song et al., 2021;Song et al., 2022;Tan et al., 2020;Kanaya et al., 2000;Kanaya et al., 2007;Li et al., 2019). The impact of HO_2 uptake chemistry on radical concentration is different under different environmental conditions (Whalley et al., 2015;Mao et al., 2010;Li et al., 2019). To evaluate the contribution of HO_2 uptake chemistry to radical concentrations in this study, we coupled HO_2 heterogeneous uptake into the base model (RACM2-LIM1) and conducted three sensitivity experiments, as shown in R1 and Eq. (3).

$$HO_2 + \text{aerosol} \rightarrow \text{products} \qquad \text{R1}$$

$$k_{HO_2+\text{aerosol}} = \frac{\gamma * \text{ASA} * \nu_{\text{HO}_2}}{4} \qquad (3)$$

where ASA [μm^2 cm^{-3}], which represents the aerosol surface area concentration, can be estimated by multiplying the mass concentration of $PM_{2.5}$ [μg m^{-3}] by 20 here because there were no direct ASA observations in this campaign (Chen et al., 2019;Wang et al., 2017). ν_{HO_2}, which can be calculated by Eq. (4), refers to the mean molecular velocity of HO_2 with a unit of cm s^{-1}.

$$\nu_{\text{HO}_2} = \sqrt{\frac{8 * \text{R} * \text{T}}{0.033 * \Pi}} \qquad (4)$$

where T [K] and R [J mol^{-1} K^{-1}] denote the ambient temperature and gas constant. γ, the HO_2 effective uptake coefficient, parameterizes the influence of some processes (Tan et al., 2020). γ varies in the highly uncertain range of 0-1 (Song et al., 2022), and is the most critical parameter to impact HO_2 uptake chemistry. Only several observations of γ have been reported (Taketani et al., 2012;Zhou et al., 2021;Zhou et al., 2020). The measured γ at the Mt. Tai site and Mt. Mang site were 0.13-0.34 and 0.09-0.40, respectively (Taketani et al., 2012). The average value of the measured γ was 0.24 in Kyoto, Japan in the summer of 2018 (Zhou et al., 2020). Zhou et al. (2021) reported the lower-limit values for median and average values of the measured γ were 0.19 and 0.23 ± 0.21 in Yokohama, Japan in the summer of 2019. Additionally, Li et al. (2018) set 0.2 as the value of γ in the model, and Tan et al. (2020) calculated the γ of 0.08 ± 0.13 by the analysis of the measured radical budget in Wangdu.

Here, we applied the two γ (0.2 and 0.08), which have been used in the model, to evaluate the impact of HO_2 uptake on radical concentrations, as shown in Fig. 6. The modeled HO_2^* cannot match well with the observations when γ of 0.08 and 0.2 was set in the model. As the γ increased to approximately 0.3, good agreement between the modeled and observed HO_2^* concentration was achieved, demonstrating that the significant heterogeneous uptake might exist in this campaign.

It is noted that the estimated strong influence is speculative because of the uncertainties of measurements and simulations. Overall, the γ evaluated in this study was comparable with those observed at the Mt. Tai and Mt. Mang in China, and Kyoto and Yokohama in Japan.

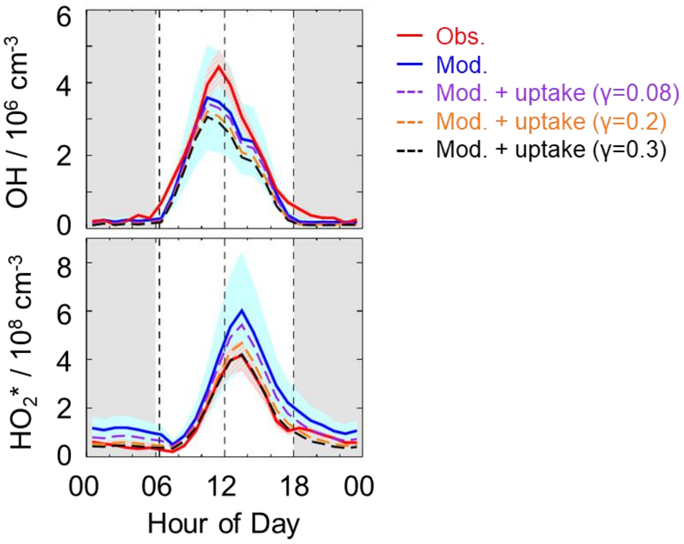

Figure 6: The diurnal profiles of the observed and modeled radical concentrations. The red and blue areas denote 1-σ uncertainties of measured and simulated radical concentrations by the base model, respectively. The orange, purple and black lines denote the simulations by the model which added the HO_2 heterogeneous uptake with different uptake coefficient. The grey areas denote nighttime.

(2) Conclusion

As for HO_2 radicals, the overestimation of HO_2^* concentration was found, indicating that HO_2 heterogeneous uptake with the effective uptake coefficient of 0.3 might make a significant role in HO_2 sinks.

(3) Abstract

A significant HO_2 heterogeneous uptake was found in this study, with an effective uptake coefficient of 0.3.

3. Previous specific point #11:

   The authors stated "over 100% conversion rate" of HO_2 in the reply and in L116 of the ATC version. I believe this measurement of the conversion efficiency is done in the environment where HO_2 is only present (i.e., RO_2 is not) and wonder how this over 100% conversion is measured.

Reply

The measurement of the conversion efficiency is done in the environment where RO_2 is not present. We calculated the HO_2 conversion by the calibration source. In the calibration experiments of PKU-LIF, we set two different modes, which are HOx mode and HO_2 mode. Photolysis of water molecules at 185 nm leads to the production of OH radical and H atom and it is generally assumed that the H-atoms are completely converted to HO_2 radical. In this mode, equal amounts of OH and HO_2 radicals are present simultaneously, and it is called HOx mode. The OH signal (C^*) includes the OH from the water photolysis (C_1) and the OH which is converted by HO_2 and NO in the detection cell (C_2).

In another mode, CO is added as an OH scavenger, in order to convert all OH to HO_2 between photolytical generation and intake into the detection cell, which is called HO_2 mode. In this mode, OH is converted to HO_2 by CO in the calibration cell. The amounts of HO_2 from the water photolysis and the HO_2 converted by OH via CO are equal, which are equal to the OH from the water photolysis separately. The total OH signal ($C^\#$) in this mode denotes the sum OH which is converted by the HO2 radicals from the water photolysis and by the HO2 radicals from the reaction of OH and CO, and thus the OH signal which is converted by HO_2 from the water photolysis is $C^\#/2$.

The HO_2-to-OH conversion efficiency (V) can be denoted by the ratio of the OH signal which is converted by HO_2 and NO in the detection cell (C_2) to the HO_2 from the water photolysis which is equal to the OH from the water photolysis (C_1). Besides, C_2 in HOx mode is equal to $C^\#/2$ in HO_2 mode, and C_1 in HOx mode is equal to the difference between C^* and C_2. Therefore, the conversion efficiency (V) is calculated according to the Eq. (1).

$$V = \frac{C_2}{C_1} = \frac{C^\#/_2}{C^* - C_2} = \frac{C^\#/_2}{C^* - C^\#/_2} \qquad (1)$$

In this campaign, NO mixing ratios were switched between 25 ppm (low NO mode) and 50 ppm (high NO mode). We calculated the HO_2-to-OH conversion efficiency in low and high NO modes according to Eq. (1). In high NO mode, the value of C_2 was larger than the value of C_1, indicating the reactions of RO_2 and NO lead to the additional OH signal.

In the manuscript, we stated 'over 100% conversion rate' was not accurate, and we replaced the expression with 'while those in high NO mode reached 100%'.

Revision

HO_2-to-OH conversion efficiencies in low NO mode ranged within 80%-95%, while those in high NO mode reached 100%, demonstrating that the high NO concentration is sufficiently to achieve complete HO_2 to OH conversion and thus the HO_2 measurement was affected by RO_2 radicals.

4. Previous specific point #17:

   Though defined in L508, it is not clear if OVOCs (and CO) are included in the AOC_VOCs or not. This will affect the interpretation of the ozone yield per VOCs oxidation as about 2.

Reply

In the previous response, the AOC_{VOCs} include the AOC derived from the oxidation of CO and OVOCs besides VOCs. Herein, we redefine the AOC_{VOCs}, which denote the channels of primary VOCs (excluding OVOCs, and mainly alkanes, alkenes, aromatics and isoprene) with OH radicals. The figure 7 (c-d) and the related descriptions were revised in the revised manuscript.

Revision

Herein, we presented the NO dependence on $P(O_3)_{net}$, AOC_{VOCs}, and the ratio of $P(O_3)_{net}$ to AOC_{VOCs} in Fig. 8 (b-d), in which AOC_{VOCs} denotes the atmospheric oxidation capacity only from the VOCs oxidation, which includes the channels of primary VOCs (excluding OVOCs, and mainly alkanes, alkenes, aromatics and isoprene) with OH radicals.

An upward trend of $P(O_3)_{net}$ was presented with the increase of NO concentration when NO concentration was below 1 ppb, while $P(O_3)_{net}$ decreased with the increase of NO concentration because NO_2 became the sink of OH radicals gradually when NO concentration was above 1 ppb. In terms of the NO dependence on AOC_{VOCs}, no significant variation was found, indicating VOCs oxidation was weakly impacted by NO concentrations in this campaign. Since AOC_{VOCs} can represent the VOCs oxidant rate, and thus the ratio of $P(O_3)_{net}$ to AOC_{VOCs} can reflect the yield of net ozone production from VOCs oxidation. Similar to $P(O_3)_{net}$, the ratios increased with the increase of NO concentration when NO concentration was below 1 ppb, while the ratios decreased with the increase of NO concentration when NO concentration was above 1 ppb, indicating the yield of net O_3 production from VOCs oxidation would be lower within the low NO regime (< 1 ppb) and high NO regime (> 1 ppb). The median ratios ranged from 1.0 to 4.5, and the maximum of the median ratios existed when NO concentration was approximately 1 ppb, with a value of approximately 4.5. The nonlinear response of the yield of net ozone production to NO indicated that it is necessary to optimize the NOx and VOC control strategies for the reduction of O_3 pollution effectively.

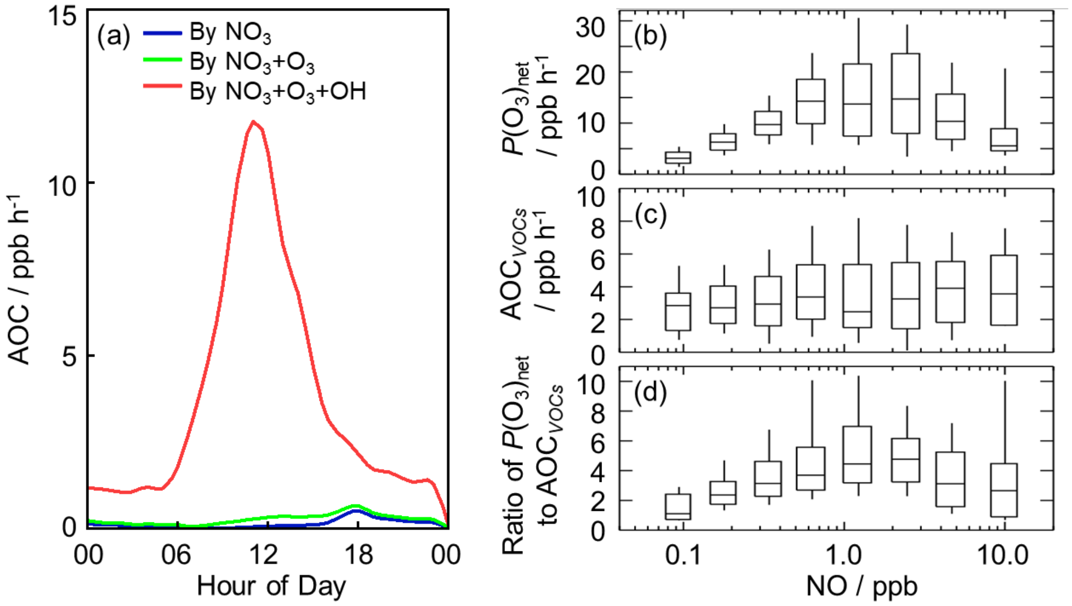

Figure 8: (a) The diurnal profiles of AOC in this campaign. (b) NO dependence on $P(O_3)_{net}$ during the daytime. (c) NO dependence on AOC_{VOCs} during the daytime, and AOC_{VOCs} denotes the atmospheric oxidation capacity only from the VOCs oxidation. (d) NO dependence on the ratio of $P(O_3)_{net}$ to AOC_{VOCs} during the daytime. The box-whisker plots in (b-d) give the 10%, 25%, median, 75%, and 90% $P(O_3)_{net}$, AOC_{VOCs} and the ratio of $P(O_3)_{net}$ to AOC_{VOCs}, respectively.

5. Previous specific point #17:

   The new statement from L514 (ATC version), "When NO concentration was above 1 ppb, the ratio decreased with the increase of NO concentration because NO_2 became the sink of OH radicals gradually." is wrong. The statement would be valid with AOC, but is not with AOC_VOC.

Reply

Thanks for your helpful suggestions. We revised the description of figure 7 (b-d) as follows.

Revision

An upward trend of $P(O_3)_{net}$ was presented with the increase of NO concentration when NO concentration was below 1 ppb, while $P(O_3)_{net}$ decreased with the increase of NO concentration because NO_2 became the sink of OH radicals gradually when NO concentration was above 1 ppb. In terms of the NO dependence on AOC_{VOCs}, no significant variation was found, indicating VOCs oxidation was weakly impacted by NO concentrations in this campaign. Since AOC_{VOCs} can represent the VOCs oxidant rate, and thus the ratio of $P(O_3)_{net}$ to AOC_{VOCs} can reflect the yield of net ozone production from VOCs oxidation. Similar to $P(O_3)_{net}$, the ratios increased with the increase of NO concentration when NO concentration was below 1 ppb, while the ratios decreased with the increase of NO concentration when NO concentration was above 1 ppb, indicating the yield of net O_3 production from VOCs oxidation would be lower within the low NO regime (< 1 ppb) and high NO regime (> 1 ppb). The median ratios ranged from 1.0 to 4.5, and the maximum of the median ratios existed when NO concentration was approximately 1 ppb, with a value of approximately 4.5. The nonlinear response of the yield of net ozone production to NO indicated that it is necessary to optimize the NOx and VOC control strategies for the reduction of O_3 pollution effectively.

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Response to Reviewer comment #3:

General comments:

In this revision, the authors have attempted to address my original comments regarding 1) the agreement between the modeled and measured OH concentrations, 2) interferences with their OH measurements, 3) interferences with their HO_2 measurements, and 4) their rate of ozone production analysis. While the revisions have improved the manuscript, there are still several issues related to the above that still need to be addressed prior to publication.

Reply

Thanks for your helpful comments which would help us to improve the manuscript. We have taken all these suggestions into account and have made corrections in this revised manuscript. Below are our responses to the specific comments, highlighted in blue, with changes to the manuscript highlighted in green.

Specific comments:

1. As suggested in my original review, the authors have added uncertainty estimates to Figure 3 that illustrate that on average the measured OH concentrations agree with modeled concentrations. They have also attempted to justify their conclusion that the measured concentrations are significantly greater than the model, illustrating in their response that on days when NO was less than 0.2 ppb that the measured concentrations were greater than the model considering the 1 sigma uncertainty of both the measurements and the model. It would be more convincing to the reader to demonstrate significance at the 95% (2-sigma) confidence level. Perhaps plotting the observed-to-modeled ratio as a function of NO with propagating the measurement and model errors would provide a better illustration, similar to Figure 11 in Tan et al., 2018.

   However, as mentioned in my original review, the agreement between the measurements and the model for this study is much better than that for the previous measurements highlighted in the paper, such as the factor of 3-5 found by Hofzumahaus et al. (2009). As I mentioned previously, the paper would benefit from an expanded discussion of why the agreement appears to be much better in this study compared to the other studies. Why is the mixing ratio of "X" required to match the OH measurements much less than that needed at some of the other sites?

Reply

As your suggestions, we added the NO dependence on the HOx observed-to-modeled ratio to provide a better illustration of the comparison between HOx observations and simulations in Section 4.2.1.

As for the comparison of missing OH sources between this study and other campaigns, we added some discussion in Section 4.2.2.

Revision

(1) Section 4.2.1

The NO dependence on observed and modeled HOx concentrations and the NO dependence on HOx observed-to-modeled ratios were illustrated in Fig. 5 and Fig. S4.

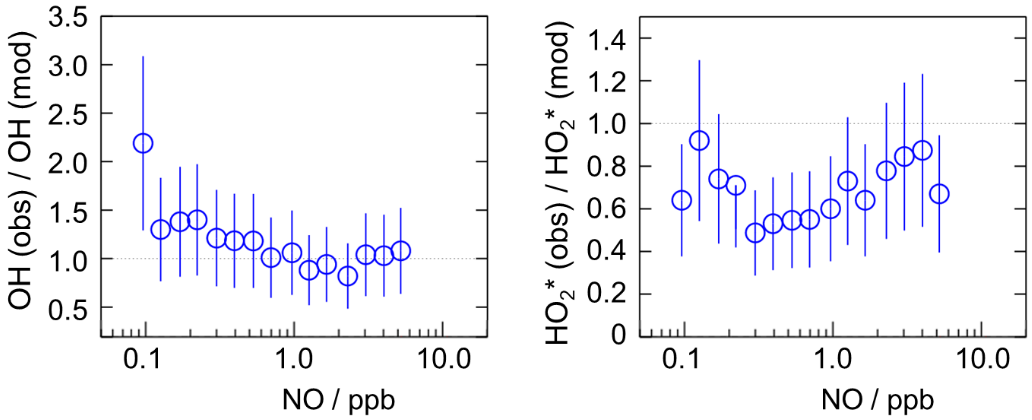

Figure S4: NO dependence on the ratios of HOx observations to simulations for daytime conditions. The vertical lines denote the combined uncertainty from radical measurements and model calculations via error propagation.

(2) Section 4.2.2

Compared to the Shenzhen site, the X concentration in the Backgarden and Heshan sites in PRD was higher, which might be affected by the different air masses in the three sites. The k_{OH} in the Shenzhen site was much lower than those in Backgarden and Heshan sites, and a weaker variation of k_{OH} in Shenzhen was observed. Under the influence of the East Asian monsoon, the prevailing wind for the PRD area is mostly southerly during the summer months and mostly northerly during the winter months (Fan et al., 2005;Zhang et al., 2008). The Backgarden site is located in Guangzhou, and the Heshan site is located in Jiangmen. The two cities are along the north-south axis, and thus the air masses of the Backgarden and Heshan sites are intimately linked with each other, while the air mass in Shenzhen is more similar to Hongkong (Zhang et al., 2008).

Compared to the VOCs reactivity in the air mass at Backgarden and Yufa sites reported by Lu et al. (2013), lower isoprene reactivity and OVOCs reactivity were observed in Shenzhen site. As discussed in Section 4.2.1, the OH underestimation might be closely related to the composition of VOCs reactivity. Therefore, further exploration of this unclassical OH recycling is needed to improve our understanding of radical chemistry, especially the mechanisms related to isoprene and OVOCs.

2. Related to this, it is also not clear whether the difference between the modeled loss of OH and the measured rate of production illustrated in Figure 4 is significant. The authors should add the estimated and propagated uncertainty associated with the modeled loss and calculated production in order to demonstrate that their proposed missing OH source is significant.

Reply

Thanks for your helpful suggestions. We added the uncertainty in Fig. 4, and revised the description of Fig. 4.

Revision

As shown in Fig. 4 (b), the discrepancy between the OH production and destruction rates at around 11:00-15:00, which was approximately of (3.1~4.6) ppb h^{-1}, cannot be explained by the combined experimental uncertainties. The discrepancy was attributed to the missing OH sources because k_{OH} was constrained in this study.

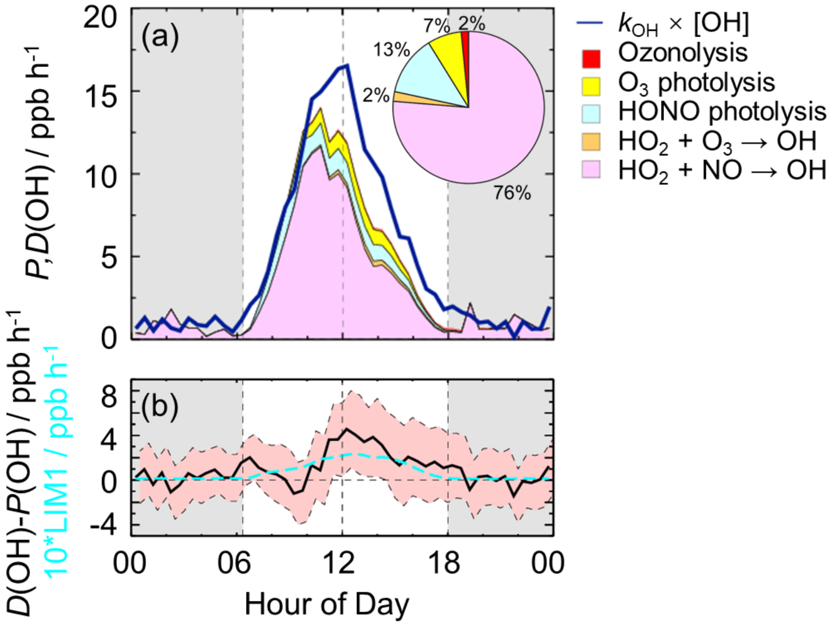

Figure 4: (a) The diurnal profiles of OH production and destruction rates and the proportions of different known sources in the calculated production rate during the daytime. The blue line denotes the OH destruction rate, and the colored areas denote the calculated OH production rates from the known sources. (b) The missing OH source which was the discrepancy between the OH destruction and production rates, and the OH production rate which was ten times the production rate derived from LIM1 mechanism. The red shaded areas denote the combined uncertainty from the experimental errors of the measured quantities (Table S1) and the reaction rate coefficients. The grey areas denote nighttime.

3. The potential for interferences in the OH measurements still needs to be considered. Unfortunately, I misspoke in my previous review regarding the impact of potential interferences on the agreement between the modeled and measured OH. Since the authors did not test for interferences, the measured OH concentrations should be considered an upper limit to the actual OH concentrations, and the presence of an interference could explain the discrepancy between the measurements and the model. While the authors provide some evidence that an interference from the ozonolysis of alkenes may not have impacted their measurements, other interferences may have impacted their measurements such as the decomposition of trioxides inside their detection cell, especially under low NO

conditions (see Fittschen et al., Atmos. Chem. Phys., 19, 349-362, 2019). While it may be true that the measurements are free from interferences, the authors should at least acknowledge that unmeasured interferences could contribute to the discrepancy with the model results.

Reply

Thanks for your suggestions, we conducted sensitivity experiments to explore the impact of trioxides (ROOOH) on radical concentrations. Herein, we integrated the reactions of the ROOOH production and destruction into the base model, as shown in Eq. (1-2).

$$RO_2 + OH \rightarrow ROOOH \quad (1)$$

$$ROOOH \rightarrow RO + HO_2 \quad (2)$$

where the RO_2 is across all RO_2 radicals in the model excluding methyl peroxy radicals, for which it has been shown that the production of a trioxide species is only a minor product channel while the trioxide yield is expected to be close to 1 for larger peroxy radicals. The rate constant of Eq. (1) is 1.5×10^{-10} cm^3 s^{-1} (Fittschen et al., 2019). In Eq. (2), the rate constant is 10^{-4} s^{-1}, leading to ROOOH lifetimes of around 3 h, of the same order as the lifetime of ROOH species (Fittschen et al., 2019).

Figure. S1 (a) presents the modeled ROOOH concentrations during this campaign, and the maximum ROOOH concentration was 4.4×10^9 cm^{-3}. The correlation of the modeled ROOOH concentrations and the ratios of OH observations to OH simulations, and the correlation of the modeled ROOOH concentrations and the difference between OH observations and simulations both demonstrated that no significant relevance between ROOOH and the underestimation of OH radicals, as shown in Fig. S1 (b-c). Additionally, the ROOOH values modeled in our another campaign (Taizhou, 2018) were comparable to or even slightly higher than the simulations in this study, and the chemical modulation tests in Taizhou confirmed the ROOOH is not a significant OH interference in our PKU-LIF system (Ma et al., 2022).

We have added the ROOOH interference in Section 2.2 in the revised manuscript and the Supplementary Information. Besides, we should note that the unmeasured interferences could contribute to the discrepancy between the radical observations and simulations.

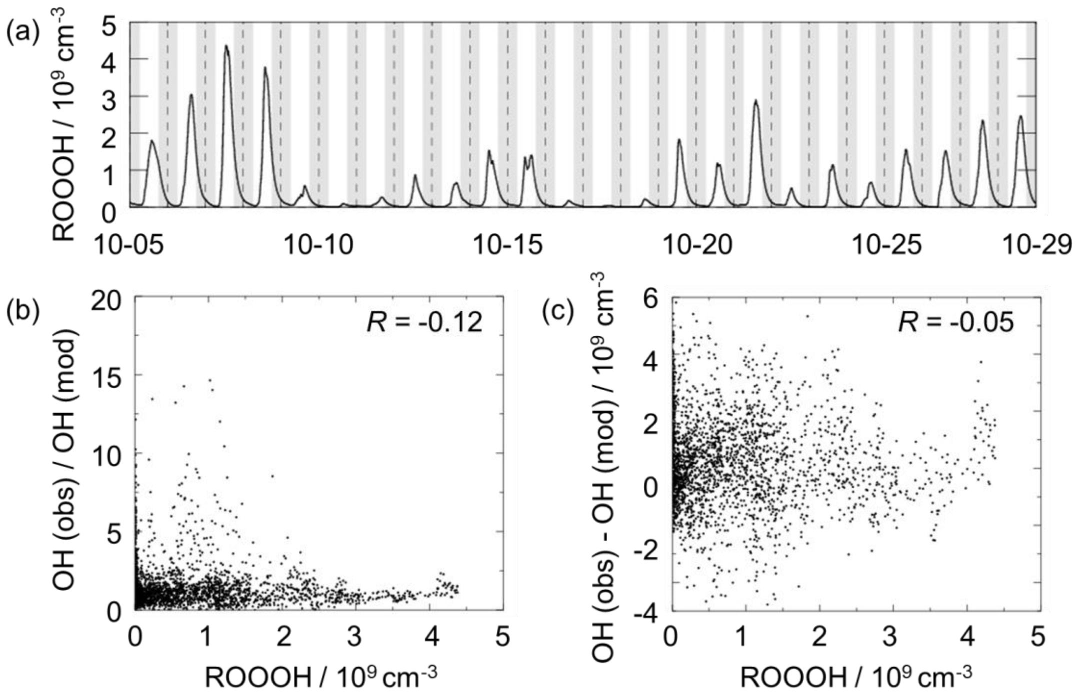

Figure S1: (a) The timeseries of ROOOH concentration from the reactions of RO_2 radicals excluding methyl peroxy radicals with OH radicals. (b) The correlation of the modeled ROOOH concentrations and the ratios of OH observations to OH simulations. (c) The correlation of the modeled ROOOH concentrations and the difference between OH observations and simulations. Only daytime values were chosen in (b-c).

Revision

(1) Section 2.2

Besides the environmental conditions, the prior studies reported that the product of the reaction of RO_2 with OH, trioxides (ROOOH), might lead to an OH interference signal. The reactions of RO_2 radicals with OH radicals might be competitive with other sinks for RO_2 radicals (Fittschen, 2019;Fittschen et al., 2019;Berndt et al., 2022). However, Fittschen et al. (2019) reported that the ROOOH interference is highly dependent on the design and measurement conditions of different FAGE instruments. Therefore, we integrated the reactions of the ROOOH production and destruction into the base model herein, with the ROOOH production rate constant of 1.5×10^{-10} cm^3 s^{-1} and the destruction rate constant of 10^{-4} s^{-1} (the details are presented in the Supplementary Information) (Fittschen et al., 2019). Figure. S1 (a) presents the modeled ROOOH concentrations during this campaign, with a maximum of about 4.4×10^9 cm^{-3}. The correlation of the modeled ROOOH concentrations and the ratios of OH observations to OH simulations, and the correlation of the modeled ROOOH concentrations and the difference between OH observations and simulations both demonstrated that no significant relevance between ROOOH and the underestimation of OH radicals, as shown in Fig. S1 (b-c). Additionally, the ROOOH values modeled in our another campaign (Taizhou, 2018) were comparable to or even slightly higher than the simulations in this study, and the chemical modulation tests in Taizhou confirmed the ROOOH is not a significant OH interference in our PKU-LIF system (Ma et al., 2022).

Overall, the OH interference during this campaign was negligible according to the analysis of the behavior of PKU-LIF system in previous campaigns, the comparison of environmental conditions between this campaign and Wangdu campaign, and the exploration of the impact of ROOOH on the discrepancy of OH observations and simulations. However, we should acknowledge that the unmeasured interference might have an effect on radical measurement. More precise chemical modulation tests are needed in the future.

(2) Figure S1 in the Supplementary Information

To evaluate the impact of the interference from ROOOH on radical concentrations, we integrated the reactions of the ROOOH production and destruction into the base model herein, as shown in Eq. (S1-S2).

$RO_2 + OH \rightarrow ROOOH$ S1

$ROOOH \rightarrow RO + HO_2$ S2

where the RO_2 is across all RO_2 radicals in the model excluding methyl peroxy radicals, for which it has been shown that the production of a trioxide species is only a minor product channel while the trioxide yield is expected to be close to 1 for larger peroxy radicals. The rate constant of Eq. (S1) is 1.5×10^{-10} cm^3 s^{-1} (Fittschen et al., 2019). In Eq. (S2), the rate constant is 10^{-4} s^{-1}, leading to ROOOH lifetimes of around 3 h, of the same order as the lifetime of ROOH species (Fittschen et al., 2019).

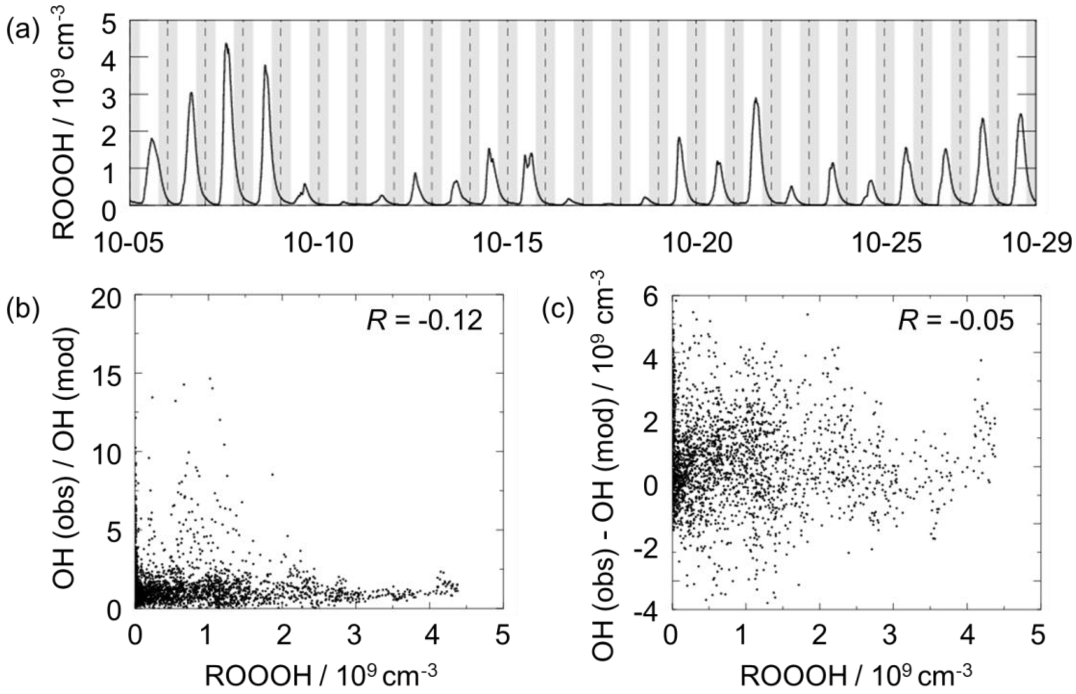

Figure S1: (a) The timeseries of ROOOH concentration from the reactions of RO_2 radicals excluding methyl peroxy radicals with OH radicals. (b) The correlation of the modeled ROOOH concentrations and the ratios of OH observations to OH simulations. (c) The correlation of the modeled ROOOH concentrations and the difference between OH observations and simulations. Only daytime values were chosen in (b-c).

4. The authors have provided additional information regarding interferences in their HO_2 measurements and have highlighted in their discussion that their measurements actually reflect HO_2^* rather than HO_2. This results in the model overestimating the measured concentrations, in contrast to the apparent agreement between the measurements and the model when the measurements were assumed to reflect only HO_2. Unfortunately, there is little discussion about this result except to say that the model may be missing heterogeneous uptake onto aerosols. Can the authors estimate the loss of peroxy radicals on aerosols and whether it could explain the discrepancy? Is this result consistent with the other studies highlighted in the paper? Given the change in the model- measurement agreement, the paper would benefit from an additional discussion related to the HO_2^* measurement and modeled discrepancy, which appears to be more significant than the discrepancy between the measured and modeled OH concentrations.

   Also, the authors state that the fact that the HO_2-to-OH conversion efficiency was greater than 100% during the high NO mode. It is not clear how this was measured. Was this measured as part of calibrations of the RO_2 conversion efficiencies? This should be clarified in the revised manuscript to give confidence in the measured and modeled HO_2^* concentrations.

Reply

Thanks for your suggestions. As for the HO_2 heterogeneous uptake, we added a new section (Section 4.3) to present the quantitative analysis in the revised manuscript.

As for the HO_2-to-OH conversion efficiency, our statement of 'the conversion efficiency was greater than 100% during the high NO mode' was not accurate, we replaced the expression with 'the conversion efficiency reached 100% during the high NO mode'. We determined the HO_2-to-OH conversion efficiency by calibrating the PKU-LIF system. In the calibration experiments of PKU-LIF, we set two different modes, which are HOx mode and HO_2 mode. Photolysis of water molecules at 185 nm leads to the production of OH radical and H atom and it is generally assumed that the H-atoms are completely converted to HO_2 radical. In this mode, equal amounts of OH and HO_2 radicals are present simultaneously, and it is called HOx mode. The OH signal (C^*) includes the OH from the water photolysis (C_1) and the OH which is converted by HO_2 and NO in the detection cell (C_2).

In another mode, CO is added as an OH scavenger, in order to convert all OH to HO_2 between photolytical generation and intake into the detection cell, which is called HO_2 mode. In this mode, OH is converted to HO_2 by CO in the calibration cell. The amounts of HO_2 from the water photolysis and the HO_2 converted by OH via CO are equal, which are equal to the OH from the water photolysis separately. The total OH signal ($C^\#$) in this mode denotes the sum OH which is converted by the HO2 radicals from the water photolysis and by the HO2 radicals from the reaction of OH and CO, and thus the OH signal which is converted by HO_2 from the water photolysis is $C^\#/2$.

The HO_2-to-OH conversion efficiency (V) can be denoted by the ratio of the OH signal which is converted by HO_2 and NO in the detection cell (C_2) to the HO_2 from the water photolysis which is equal to the OH from the water photolysis (C_1). Besides, C_2 in HOx mode is equal to $C^\#/2$ in HO_2 mode, and C_1 in HOx mode is equal to the difference between C^* and C_2. Therefore, the conversion efficiency (V) is calculated according to the Eq. (1).

$$V = \frac{C_2}{C_1} = \frac{C^{\#}/2}{C^{*}-C_2} = \frac{C^{\#}/2}{C^{*}-C^{\#}/2} \quad (1)$$

In this campaign, NO mixing ratios were switched between 25 ppm (low NO mode) and 50 ppm (high NO mode). We calculated the HO_2-to-OH conversion efficiency in low and high NO modes according to Eq. (1). In high NO mode, the value of C_2 was larger than the value of C_1, indicating the reactions of RO_2 and NO lead to the additional OH signal.

Revision

(1) HO_2 heterogeneous uptake in Section 4.3

The HO_2 heterogeneous uptake has been proposed to be a potential sink of HO_2 radicals, and thus could influence the radical chemistry and the formation of secondary pollution, especially in high-aerosol environments (Song et al., 2021;Song et al., 2022;Tan et al., 2020;Kanaya et al., 2000;Kanaya et al., 2007;Li et al., 2019). The impact of HO_2 uptake chemistry on radical concentration is different under different environmental conditions (Whalley et al., 2015;Mao et al., 2010;Li et al., 2019). To evaluate the contribution of HO_2 uptake chemistry to radical concentrations in this study, we coupled HO_2 heterogeneous uptake into the base model (RACM2-LIM1) and conducted three sensitivity experiments, as shown in R1 and Eq. (3).

HO_2 + aerosol → products R1

$$k_{HO_2+\mathrm{aerosol}} = \frac{\gamma * \mathrm{ASA} * \nu_{\mathrm{HO_2}}}{4} \quad (3)$$

where ASA [μm^2 cm^{-3}], which represents the aerosol surface area concentration, can be estimated by multiplying the mass concentration of $PM_{2.5}$ [μg m^{-3}] by 20 here because there were no direct ASA observations in this campaign (Chen et al., 2019;Wang et al., 2017). $\nu_{\mathrm{HO_2}}$, which can be calculated by Eq. (4), refers to the mean molecular velocity of HO_2 with a unit of cm s^{-1}.

$$\nu_{\mathrm{HO_2}} = \sqrt{\frac{8 * \mathrm{R} * \mathrm{T}}{0.033 * \Pi}} \quad (4)$$

where T [K] and R [J mol^{-1} K^{-1}] denote the ambient temperature and gas constant. γ, the HO_2 effective uptake coefficient, parameterizes the influence of some processes (Tan et al., 2020). γ varies in the highly uncertain range of 0-1 (Song et al., 2022), and is the most critical parameter to impact HO_2 uptake chemistry. Only several observations of γ have been reported (Taketani et al., 2012;Zhou et al., 2021;Zhou et al., 2020). The measured γ at the Mt. Tai site and Mt. Mang site were 0.13-0.34 and 0.09-0.40, respectively (Taketani et al., 2012). The average value of the measured γ was 0.24 in Kyoto, Japan in the summer of 2018 (Zhou et al., 2020). Zhou et al. (2021) reported the lower-limit values for median and average values of the measured γ were 0.19 and 0.23±0.21 in Yokohama, Japan in the summer of 2019. Additionally, Li et al. (2018)

set 0.2 as the value of γ in the model, and Tan et al. (2020) calculated the γ of 0.08±0.13 by the analysis of the measured radical budget in Wangdu.

Here, we applied the two γ (0.2 and 0.08), which have been used in the model, to evaluate the impact of HO_2 uptake on radical concentrations, as shown in Fig. 6. The modeled HO_2^* cannot match well with the observations when γ of 0.08 and 0.2 was set in the model. As the γ increased to approximately 0.3, good agreement between the modeled and observed HO_2^* concentration was achieved, demonstrating that the significant heterogeneous uptake might exist in this campaign.

It is noted that the estimated strong influence is speculative because of the uncertainties of measurements and simulations. Overall, the γ evaluated in this study was comparable with those observed at the Mt. Tai and Mt. Mang in China, and Kyoto and Yokohama in Japan.

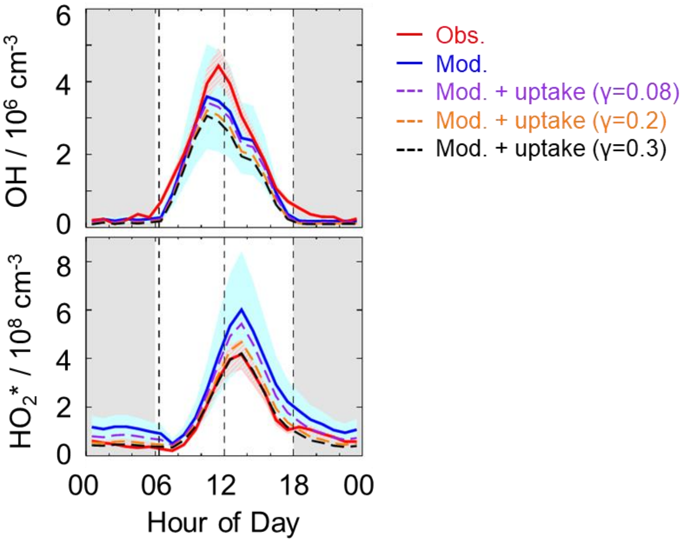

Figure 6: The diurnal profiles of the observed and modeled radical concentrations. The red and blue areas denote 1-σ uncertainties of measured and simulated radical concentrations by the base model, respectively. The orange, purple and black lines denote the simulations by the model which added the HO_2 heterogeneous uptake with different uptake coefficient. The grey areas denote nighttime.

(2) HO_2 conversion efficiency in Section 2.2

HO_2-to-OH conversion efficiencies in low NO mode ranged within 80%-95%, while those in high NO mode reached 100%, demonstrating that the high NO concentration is sufficiently to achieve complete HO_2 to OH conversion and thus the HO_2 measurement was affected by RO_2 radicals.

5. As mentioned in my previous review, the authors should clarify that their calculation of the rate of ozone production reflects the gross rate of production not the net rate, as it does not take into account the NO_2 formed that does not lead to O_3 production through the formation

of HNO_3 from the OH + NO_2 reaction. As I mentioned previously, Tan et al. (2017) used the net rate of ozone production in their analysis of the chemistry at the Wangdu site. Note the difference between equation 5 in Tan et al. (2017) and equation 3 in this paper. In contrast, Tan et al. (2018) calculated the gross rate of ozone production in equation 6 in their paper. These differences should be clarified as the authors still compare their estimated rates of ozone production to the results from both the Tan et al. 2017 and Tan et al., 2018 (lines 438-439 of the revised manuscript).

Reply

Thanks for your helpful suggestions. The reaction of NO_2 and OH was missed in equation 5 (equation 7 in the revised version) in the previous response and we have revised the equation 5 (equation 7 in the revised version) in the revised manuscript. However, in the calculation of $P(O_3)$ in the previous response, we included the reaction of OH and NO_2, as shown in the figure S7 in the revised Supplementary Information. Thus, the values of $P(O_3)$ in the previous response has denoted the net O_3 production rate, and the Fig. 8 (b) was not be changed.

Overall, in Section 4.5 'AOC evaluation', the $P(O_3)$ in equation 5 (equation 7 in the revised version) was revised. Besides, the comparison between the O_3 production rate in this study and that in other studies was revised. Additionally, the Fig. 8 (c-d) was revised, because we redefine the AOC_{VOCs}. We included the AOC derived from CO and OVOCs in AOC_{VOCs} in the previous response, and herein, we only included the AOC derived from primary VOCs (excluding OVOCs, and mainly alkanes, alkenes, aromatics and isoprene) in AOC_{VOCs}.

Revision

(1) In the revised version, we revised the equation 7, and the equation 5-6 were not be changed.

$$F(O_3) = k_{HO_2+NO}[HO_2][NO] + \sum_i k_{RO_2i+NO}[RO_2]_i[NO] \tag{5}$$

$$L(O_3) = \theta j(O^1D)[O_3] + k_{O_3+OH}[O_3][OH] + k_{O_3+HO_2}[O_3][HO_2] +$$

$$(\sum(k^i_{alkenes+O_3}[alkenes^i]))[O_3] \tag{6}$$

$$P(O_3)_{net} = F(O_3) - L(O_3) - k_{NO_2+OH}[NO_2][OH] \tag{7}$$

(2) The comparison between the O_3 production rate in this study and that in other studies.

The modeled $P(O_3)_{net}$ was comparable to the net O_3 production rate in Wangdu site in summer (Tan et al., 2017), while it was much higher than the O_3 production rate in Beijing in winter despite being the gross production rate (Tan et al., 2018).

(3) We revised the figure 8 (c-d) and the descriptions.

Herein, we presented the NO dependence on $P(O_3)_{net}$, AOC_{VOCs}, and the ratio of $P(O_3)_{net}$ to AOC_{VOCs} in Fig. 8 (b-d), in which AOC_{VOCs} denotes the atmospheric oxidation capacity only from the VOCs oxidation, which includes the channels of primary VOCs (excluding OVOCs, and mainly alkanes, alkenes, aromatics and isoprene) with OH radicals.

An upward trend of $P(O_3)_{net}$ was presented with the increase of NO concentration when NO concentration was below 1 ppb, while $P(O_3)_{net}$ decreased with the increase of NO concentration because NO_2 became the sink of OH radicals gradually when NO concentration was above 1 ppb. In terms of the NO dependence on AOC_{VOCs}, no significant variation was found, indicating VOCs oxidation was weakly impacted by NO concentrations in this campaign. Since AOC_{VOCs} can represent the VOCs oxidant rate, and thus the ratio of $P(O_3)_{net}$ to AOC_{VOCs} can reflect the yield of net ozone production from VOCs oxidation. Similar to $P(O_3)_{net}$, the ratios increased with the increase of NO concentration when NO concentration was below 1 ppb, while the ratios decreased with the increase of NO concentration when NO concentration was above 1 ppb, indicating the yield of net O_3 production from VOCs oxidation would be lower within the low NO regime (< 1 ppb) and high NO regime (> 1 ppb). The median ratios ranged from 1.0 to 4.5, and the maximum of the median ratios existed when NO concentration was approximately 1 ppb, with a value of approximately 4.5. The nonlinear response of the yield of net ozone production to NO indicated that it is necessary to optimize the NOx and VOC control strategies for the reduction of O_3 pollution effectively.

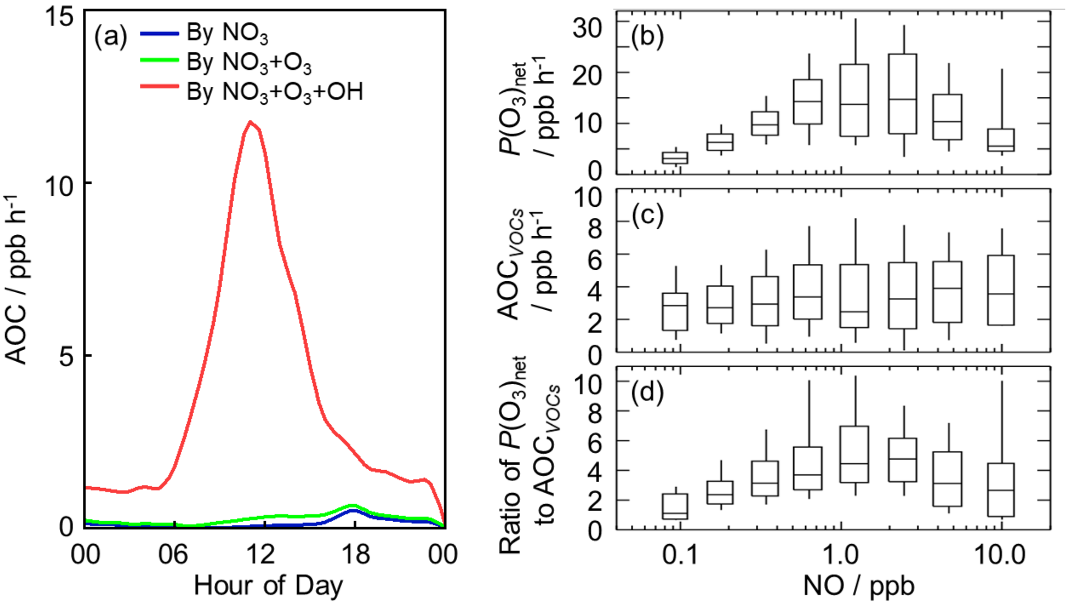

Figure 8: (a) The diurnal profiles of AOC in this campaign. (b) NO dependence on $P(O_3)_{net}$ during the daytime. (c) NO dependence on AOC_{VOCs} during the daytime, and AOC_{VOCs} denotes the atmospheric oxidation capacity only from the VOCs oxidation. (d) NO dependence on the ratio of $P(O_3)_{net}$ to AOC_{VOCs} during the daytime. The box-whisker plots in (b-d) give the 10%, 25%, median, 75%, and 90% $P(O_3)_{net}$, AOC_{VOCs} and the ratio of $P(O_3)_{net}$ to AOC_{VOCs}, respectively.

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