We appreciate the reviewers' insightful comments and constructive suggestions, which will help us to provide a more accurate description of our work. Our responses are detailed below, presented in red, following the reviewers' comments that are in black. The revisions made to the manuscript are highlighted in yellow.

#### **Response to reviewer # 1:**

**Review for: Measurement report: Vertical and temporal variability of nearsurface ozone production rate and sensitivity in an urban area in Pearl River Delta (PRD) region, China.** 

In this manuscript, the authors have presented a detailed study on ozone production rates in an urban area in the Pearl River Delta region of China, including an investigation into the vertical and temporal variability of ozone, it's production rate and its precursors. The subject area is in the scope of this journal and would be of interest to the urban air quality community. I would recommend this manuscript for publication, provided the following comments have sufficiently been addressed.

We are honored by your positive evaluation of our manuscript. Thanks for your recognition of this study's potential contribution to the urban air quality community. We have taken your feedback with the utmost seriousness and have revised the manuscript to ensure that all points are considered.

## **Overall comments:**

I am not completely convinced that comparing measured and modelled O3 mixing ratios is a good way to validate the model, or to decide on any dilution factors (e.g Line 601). Measured O<sub>3</sub> mixing ratios will be influenced by transport, whereas modelled O<sub>3</sub> will not so you cannot draw a direct comparison here. In my opinion, the authors should address the caveats with using this to method to derive your dilution rates in the text more clearly or use a different compound which is formed from secondary chemistry, such as glyoxal, to determine their dilution rates / model lifetimes. Alternatively, they could use a value quoted in the literature and discuss the caveats of this instead. However, comparing measured  $PO_3$  vs modelled  $PO_3$ seems reasonable.

Thank you for the insightful suggestions. Unfortunately, we haven't measure glyoxal during the observation campaign. The dilution factors may only partially reflect the impact of physical transport on  $O<sub>3</sub>$  mixing ratios, particularly the outflow of  $O_3$  from the observation site due to physical processes. We have added the caveats regarding the use of the comparison between measured and modelled O<sup>3</sup> to derive the dilution rates in lines 596-598:

"Previous studies have utilized the comparison of measured and modelled  $O<sub>3</sub>$ concentrations to determine the dilution factor in modelling studies, discovering that suitable dilution factors vary by location (Yang et al., 2021)."

and lines 602-605 in the modified manuscript:

"However, given that  $O_3$  concentrations are affected by physical transport processes, the dilution factor might only represent the outflow of  $O<sub>3</sub>$  from the observation site. Therefore, there may be limitations in using this method for precise comparisons." To make the description more accurate, we have also changed the sentence in lines 292-294 in the original text: "The effect of physical processes (such as vertical and horizontal transport) was considered by setting a constant dilution factor of 1/43200 s<sup>-1</sup> throughout the modelling period." to "To avoid the build-up of long-lived species to unreasonable levels, we also considered the physical dilution process by setting a constant dilution factor of  $1/43200 s^{-1}$  throughout the modelling period (Liu et al., 2021; Decker et al., 2019).<sup>"</sup> in lines 295-298 in the modified manuscript.

Furthermore, we conducted a comparison between the measured and modelled  $P(O_X)_{net}$  under different dilution rates, the results show that the modelled  $P(O_3)_{net}$ first increases and then decreases as the dilution factor decreases, which corresponds to an extension of the species' lifetime. Notably, the best agreement between the modelled and modelled  $P(O_3)_{net}$  was achieved when the species lifetime was set to 12 h. This discussion has been integrated into the revised manuscript in lines 605-613:

"We further compared the measured and modelled  $P(O_3)_{net}$  under different dilution factors. The modelled  $P(O_3)_{net}$  initially increases and then decreases as the dilution factor decreases (equivalent to an increase of species lifetime). However, the influence of varying dilution rates on the modelled  $P(O_3)_{net}$  is minimal, constituting less than  $30\%$ , due to the short lifetimes of the HO<sub>2</sub> and RO<sub>2</sub> radicals, which determine the *P*(O<sub>3</sub>)<sub>net</sub> values (Wang et al., 2021). Notably, the modelled *P*(O<sub>3</sub>)<sub>net</sub> closely matched the measured values when the species lifetime was set to 12 h, as illustrated in Fig. S3b. Consequently, a constant dilution factor of  $1/43200$  s<sup>-1</sup> was applied throughout the observation period."

The authors need to be much clearer why understanding the vertical distributions are important to the air quality community. It seems that daytime  $O_3$  is well mixed, and so ground level  $\Omega_3$  measurements would be representative of the vertical column. Is the key message that although this is the case, the VOC profile is different at different heights, meaning that if the chemical box modelling community is constraining to ground-level concentrations, they may not be accurately representing in situ O3 production in the vertical column? If this is the case, it would be a very interesting conclusion and should be outlined in the text.

We concur with your opinion that the ozone  $(O_3)$  concentrations are well mixed in the boundary layer during daytime hours. However, the  $O<sub>3</sub>$  formation mechanisms exhibited significant vertical variability, driven by fluctuations in the concentrations of volatile organic compounds (VOCs) and nitrogen oxides (NOx). Chemical box modelling, when solely constrained by ground-level measurements, fails to accurately reproduce the  $O_3$  production across the vertical column. Consequently, relying solely on ground-level  $O_3$  formation mechanisms to devise control strategies for ozone precursors is inadequate. A more comprehensive approach is necessary to effectively address the complexities of  $O<sub>3</sub>$  production throughout the atmospheric column. We have outlined this conclusion in lines 488-496 in Sect. 3.1.2 in the modified manuscript:

"In conclusion, our daytime observations revealed minimal vertical gradients in the concentrations of  $O_3$ ,  $NOx$ ,  $Ox$ , and TVOC, attributed to the rapid vertical mixing effects driven by surface heating effects (Tang et al., 2017). This suggests that groundlevel  $O_3$  concentrations would be representative of the entire vertical column. Nonetheless, the OFP varies for different VOCs profiles at various heights, and the vertical mixing effects facilitates the downward transport of  $O<sub>3</sub>$  photochemically formed from higher altitudes to the near-ground layer. Consequently, a box model constraining to ground-level NOx and VOCs concentrations may not accurately reflect the in situ  $O_3$  production in the vertical atmospheric column." as well as lines 878-887 in the conclusion section:

"The findings provide us in-depth understanding of near-ground vertical variability in O<sub>3</sub> formation mechanisms, which are influenced by the concentrations of VOCs and NOx, and the distinct OFP associated with different VOCs profiles. During daytime, the vertical mixing of air masses is substantially enhanced due to the effect of surface heating. Consequently, photochemically formed  $O_3$  at higher altitudes can be vertically transported downward to the near-ground layer. Under this condition, control strategies for  $O_3$  precursors based on the  $O_3$  formation mechanisms on the ground-level are insufficient. A more comprehensive approach is necessary to effectively address the complexities of  $O_3$  production throughout the atmospheric column. The vertical variability of  $O_3$  formation mechanisms should be taken into account when making effective  $O_3$  control strategies in the PRD area of China."

### **Minor comments:**

Line 44: Type, "either" included twice. Remove one instance.

Ok, we removed one "either" in the modified manuscript.

Line 190: Do you mean Table S3? At first, I went to figure S3 but I think you meant table S3. Please clarify in the text.

We actually meant Sect. S3 in the supplementary materials: "**S3. The experiments concerning the light-enhanced loss of O3**" We added Sect. S3 in the main text.

Line 203: Same as above comment – do you mean Table S4?

We actually meant Sect. S4 in the supplementary materials: "**S4. Measurement error of** *P***(O3)net and the LOD of the NPOPR detection system**" We added Sect. S4 in the main text.

Line 232: Please clarify why you only used VOCs measured during the  $H_3O^+$  mode. The PTR-ToF-MS instrument, when operated at NO+ mode, primarily detects higher alkanes, which significantly contribute to the formation of secondary organic aerosols (SOA) but negligible contributions to photochemical  $O<sub>3</sub>$  formation (Wang et al., 2020). Therefore, only the VOCs species identified during the PTR-ToF-MS measurements in  $H_3O^+$  mode were used in this study. We have added this explanation in the main text in lines 232-234:

"Operating the PTR-ToF-MS instrument in NO<sup>+</sup> mode primarily detects higher alkanes, which are known significantly contribute to the formation of secondary organic aerosols (SOA) but negligible contributions to photochemical  $O_3$  formation (Wang et al., 2020)."

Line 288: I wouldn't call these "conventional" pollutants. Please rephrase. Perhaps "inorganic pollutants"?

We agree with the reviewer, we changed it to "inorganic gaseous pollutants".

Line 295: Please clarify how you have decided on these background concentrations. Can you reference anywhere else this has been used?

We have set the background concentrations of  $O_3$ , CO, and CH<sub>4</sub> according to the findings of Wang et al. (2011), Wang et al. (2022a), and WMO greenhouse gas bulletin (2022), respectively. We have cited these references accordingly in the main text (lines 300-301):

"Additionally, the dry deposition rate of  $O_3$  was set to 0.42 cm s<sup>-1</sup>, and the background of  $O_3$ , CO, and CH<sub>4</sub> were set to 30, 70, and 1800 ppby, respectively, **based on the** findings of Wang et al. (2011), Wang et al. (2022a), and WMO greenhouse gas bulletin  $(2022).$ "

Line 377: Now referred to as "ozone" in the text. It's better to ensure that either "O<sub>3</sub>" or "ozone" is used consistently throughout the text.

We have changed "ozone" to "O<sub>3</sub>" throughout the manuscript, after defining it on line 55: "Tropospheric ozone  $(O_3)$ , which has adverse effects on ecosystems, climate change, and human health…"

Line 400: In Table 1, episode II O<sub>3</sub> mixing ratios are lower than non-episode II O<sub>3</sub> mixing ratios. Please explain why this is the case in the text.

Through the average O3 mixing ratio during episode II was lower than during nonepisode II, the variability of these average values, as indicated by the standard deviation, is actually higher during episode II. This means that even though there are days with very high hourly average  $O_3$  concentrations-which define  $O_3$  pollution episodes, where levels exceed the Grade II standard of 102 ppbv-the overall average  $O_3$  concentrations for episode II is not higher than that of non-episode II, it shows greater fluctuations, as suggested by the larger standard deviation. We have added the explanation in lines 413-419 in the revised manuscript:

"For example, through there are days with very high hourly average  $O_3$  concentrations which define  $O_3$  pollution episodes-where levels exceed the Grade II standard of  $102$ ppby-the overall average  $O_3$  concentrations for episode II is not higher than that of non-episode II. This suggests that despite the occurrence of peak hourly levels, the average concentration for episode II remains lower, highlighting the fluctuating pattern of  $O_3$  levels during these episodes."

Line 784: I'm confused on which VOCs fall into which categories. I looked at Table S2 (although if that is where the reader should be looking, please direct them here in the text), and many of the VOCs fall under two categories (e.g. AVOC and NMHC). Does that mean some species are repeated in different categories in Figure 9?

Yes, we categorized the VOCs according to Table S2, and many of the VOCs fall under two categories. Therefore, the VOCs species in different categories in Figure 9 might be repeated. We have added this explanation on lines 745-747 in the modified manuscript:

"The VOCs species, categorized into different precursor groups as listed in Table S2, indicate that some species depicted in Figure 9 may appear in multiple categories and hence could be repeated."

Line 820: It would be nice to know which specific AVOCs/OVOCs might be key, so that potential sources that can be targeted for reduction could be identified. The conclusion to this section is fine, but very general and doesn't really add any new details.

Thanks for your suggestion. However, in our study, we have lumped the individual AVOCs/OVOCs species together to assess their relative incremental reactivity (RIR). This approach does not allow us to analyze which specific AVOCs or OVOCs are the most critical in terms of RIR. Alternatively, we have identified and presented the three VOC species with the highest OFP in Table S4, distinguishing between episodes and non-episodes. We acknowledged and discussed the significance of pointing these key species for targeted reduction strategies in the revised manuscript in lines 786-797:

"Given that photochemical  $O_3$  formation is most sensitive to AVOC and OVOC groups, we further identified and presented the three VOC species with the highest OFP during different episodes and non-episodes in Table S4. Results show that compounds such as toluene, *m/p*-xylene, and n-butane in AVOC group, formaldehyde, hydroxyacetone, and ethanol in OVOC group have identified as the most significant contributors to the total OFP in all episodes and non-episodes. Toluene, *m/p*-xylene, and n-butane are often associated with specific industrial processes (Shi et al., 2022; Liang et al., 2017), while formaldehyde, hydroxyacetone, and acetaldehyde can originate from both the industrial processes and natural sources (Parrish et al., 2012; Fan et al., 2021; Spaulding et al., 2003; Salthammer 2023). Priority of these emission sources should be given to reducing AVOC and OVOC to mitigate O<sub>3</sub> pollution in the PRD area of China."

Line 841: "The TVOC and OFP exhibited variable trends with increased height during both daytime and nighttime" – what are the implications of this to the modelling or measurement community?

As mentioned above, we have added more discussion concerning the variable OFP for different VOCs profiles at various heights in lines 492-496 in Sect. 3.1.2 in the modified manuscript:

"Nonetheless, the OFP varies for different VOCs profiles at various heights, and the vertical mixing effects facilitates the downward transport of  $O<sub>3</sub>$  photochemically formed from higher altitudes to the near-ground layer. Consequently, a box model constraining to ground-level NOx and VOCs concentrations may not accurately reflect the in situ  $O_3$  production in the vertical atmospheric column."

And further added the implications to the modelling or measurement community in lines 820-821 in the revised manuscript:

"However, the TVOC and their OFP exhibited variable trends with increased height during both daytime and nighttime, observed in episodes and non-episodes, which indicates the complexities of  $O<sub>3</sub>$  formation mechanisms at different heights throughout the atmospheric column."

Line 847: I don't think you performed a test for statistical significance in this part, so perhaps rephrase.

Sorry for the inaccurate description. We meant the mean concentrations of  $O<sub>3</sub>$ precursors, including CO, NO, NO2, and TVOC, were not necessarily higher during episodes than those during non-episodes. We have changed this sentence to "The mean concentrations of  $O_3$  precursors, including CO, NO, NO<sub>2</sub>, and TVOC, were not consistently elevated during episodes compared to their levels during non-episodes."

Line 899: Could you expand a bit more in your conclusions on why an in-depth understanding of vertical variability of  $O<sub>3</sub>$  formation mechanisms is important? What could this new knowledge mean for the air quality community?

During daytime, the vertical mixing of air masses is substantially enhanced due to the effect of surface heating. Consequently, photochemically formed  $O<sub>3</sub>$  at higher altitudes can be vertically transported downward to the near-ground layer. Under this condition, control strategies for  $O<sub>3</sub>$  precursors based on the ozone formation mechanisms on the ground-level are insufficient. The vertical variability of  $O<sub>3</sub>$  formation mechanisms should be taken into account when making effective  $O<sub>3</sub>$ control strategies. We added more discussion concerning the importance of indepth understanding of vertical variability of O3 formation mechanisms in lines 878- 887 in the modified manuscript:

"The findings provide us in-depth understanding of near-ground vertical variability in O<sub>3</sub> formation mechanisms, which are influenced by the concentrations of VOCs and NOx, and the distinct OFP associated with different VOCs profiles. During daytime, the vertical mixing of air masses is substantially enhanced due to the effect of surface heating. Consequently, photochemically formed  $O_3$  at higher altitudes can be vertically transported downward to the near-ground layer. Under this condition, control strategies for  $O_3$  precursors based on the  $O_3$  formation mechanisms on the ground-level are insufficient. A more comprehensive approach is necessary to effectively address the complexities of  $O_3$  production throughout the atmospheric column. The vertical variability of  $O_3$  formation mechanisms should be taken into account when making effective  $O_3$  control strategies in the PRD area of China."

## References:

Fan, J., Ju, T., Wang, Q., Gao, H., Huang, R., and Duan, J.: Spatiotemporal variations and potential sources of tropospheric formaldehyde over eastern China based on OMI satellite data, Atmos. Pollut. Res., 12, 272-285, [10.1016/j.apr.2020.09.011,](https://doi.org/10.1016/j.apr.2020.09.011) 2021.

Liang, X., Chen, X., Zhang, J., Shi, T., Sun, X., Fan, L., Wang, L., and Ye, D.: Reactivity-based industrial volatile organic compounds emission inventory and its implications for ozone control strategies in China, Atmos. Environ., 162, 115-126, [10.1016/j.atmosenv.2017.04.036,](https://doi.org/10.1016/j.atmosenv.2017.04.036) 2017.

Parrish, D. D., Ryerson, T. B., Mellqvist, J., Johansson, J., Fried, A., Richter, D., Walega, J. G., Washenfelder, R. A., de Gouw, J. A., Peischl, J., Aikin, K. C., McKeen, S. A., Frost, G. J., Fehsenfeld, F. C., and Herndon, S. C.: Primary and secondary sources of formaldehyde in urban atmospheres: Houston Texas region, Atmos. Chem. Phys., 12, 3273-3288, 10.5194/acp-12-3273-2012, 2012.

Salthammer, T.: Acetaldehyde in the indoor environment, Environ. Sci. Atmos., 3, 474-493, 10.1039/D2EA00146B, 2023.

Shi, J., Bao, Y., Ren, L., Chen, Y., Bai, Z., and Han, X.: Mass concentration, source and health risk assessment of volatile organic compounds in nine cities of Northeast China, Int. J. Environ. Res. Public Health*,* 19, 4915, 10.3390/ijerph19084915, 2022.

Spaulding, R. S., Schade, G. W., Goldstein, A. H., and Charles, M. J.: Characterization of secondary atmospheric photooxidation products: Evidence for biogenic and anthropogenic sources, J. Geophys. Res.,108, 4247, [10.1029/2002JD002478,](https://doi.org/10.1029/2002JD002478) 2003.

Wang, C., Yuan, B., Wu, C., Wang, S., Qi, J., Wang, B., Wang, Z., Hu, W., Chen, W., Ye, C., Wang, W., Sun, Y., Wang, C., Huang, S., Song, W., Wang, X., Yang, S., Zhang, S., Xu, W., Ma, N., Zhang, Z., Jiang, B., Su, H., Cheng, Y., Wang, X., and Shao, M.: Measurements of higher alkanes using NO<sup>+</sup> chemical ionization in PTR-ToF-MS: important contributions of higher alkanes to secondary organic aerosols in China, Atmos. Chem. Phys., 20, 14123-14138, 10.5194/acp-20-14123- 2020, 2020.

## **Response to reviewer # 2:**

The authors have provided additional information that answers most of the comments from my initial review (reviewer #2, report #3). However, there are still a few points that need to be addressed before publication.

We would like to express our sincere gratitude for your thorough initial review (reviewer #2, report #3) and for the time you have invested in evaluating our manuscript. We have taken your comments seriously and have made substantial revisions. We believe that these revisions have significantly improved the quality of the manuscript.

#### Major comments:

1/ Supplement S3

- The authors should clarify whether the "outdoor experiment" was carried out by flowing zero air or ambient air in the reaction and reference chambers. From the text it seems that ambient air was used.

Yes, the "outdoor experiment" was carried out by flowing zero air in the reaction and reference chambers, but the reaction and reference chambers are located outdoor. We modified the description in S3 to make it clearer:

"The light-enhanced loss of  $O_3$  in the reaction and reference chambers at 5 L min<sup>-1</sup> (the flow rate used during the observation campaign in this study) was investigated by carrying out the following outdoor experiment: the  $O<sub>3</sub>$  with a mixing ratio of approximately 130 ppby generated by the  $O_3$  generator (P/N 97-0067-02, Analytic Jena US, USA) was injected into both the reaction and reference chambers. We flowed zero air together with the generated  $O_3$  into these chambers, which are located outdoors, to ensure there was no photochemical O<sub>3</sub> production. This setup allowed us to observe the real changes in photolysis frequencies of different species during daytime."

- The authors indicate that "O3 was injected at a mixing ratio of approximately 130 ppbv …. to ensure that no photochemical O3 was produced during the outdoor experiment." – If ambient air was used during these experiments, how can the authors be sure that there is no ozone production in the chambers?

As described above, zero air is used for the tests of light-enhanced loss of  $O_3$  in the reaction and reference chambers.

#### 2/ Supplement S4

- Please clarify whether (Ox)error is an absolute or a relative error. From equation S1 it seems that this is a quadratic propagation of absolute errors.

Yes, the (Ox)error represents an absolute error, resulting from the quadratic propagation of individual absolute errors. To elucidate this concept better, we have included the following explanation in Supplement S4:

"where  $(O_X)_{error}$  represents the absolute error in the estimated  $O_X$  concentration in the reaction and reference chambers, which results from the quadratic propogation of the absolute errors  $(O_{X_{\gamma}})$  $\frac{\text{and (O}_{X_{CAPS}})}{\text{error}}$ . Here,  $\frac{\text{(O}_{X_{\gamma}})}{\text{(Cary)}}$ error denotes the error associated with the  $\gamma$ -corrected Ox of the chambers, while  $(O_{X_{CAPS}})_{error}$  signifies the measurement

error of the  $O_X$  measured by the CAPS-NO<sub>2</sub> monitor."

- The power function referenced as S2 would lead to a low error on measured Ox concentrations when [Ox]>20-30 ppb. However, it would lead to a large error for low Ox concentrations. For instance, plugging a Ox concentration of 1ppb in this equation would lead to an error of 9.7ppb, which does not seem reasonable. The authors should comment on this.

Yes, as indicated by the power function in equation S2, the error increases as the measured O<sub>X</sub> concentration decreases, resulting a more significant  $\left(O_{\chi_{\rm CAPS}}\right)_{\rm error}$  at

lower  $O<sub>X</sub>$  levels. However, this power function has been derived from the calibration for  $O_X$  concentrations ranging from 20 ppbv to 160 ppbv. Applying it outside this range, especially at very low  $O_X$  concentrations, could lead to disproportionately large errors that do not reflect the true variability of the measurement errors. In this study, the  $O<sub>x</sub>$  concentrations varied between 28 ppby and 145 ppby, which falls into the calibration range, validating the use of this power function for estimating  $\left( \mathsf{O}_{\chi_{\mathsf{CAPS}}}\right)_{\mathsf{error}}$  throughout the measurement period. We have added the related comment in Supplementary S4:

"We acknowledge that this power function has been derived from calibration data of the  $O_X$  concentrations ranged from 20 ppby to 160 ppby. Utilizing this function outside this calibrated range, especially at very low  $O_X$  concentrations, may result in errors that are disproportionately large and may not accurately capture the true variability of the measurement errors. In this study, the  $O<sub>X</sub>$  concentrations ranged from 28 to 145 ppbv, which falls into the calibration range. Consequently, this power function is deemed appropriate for estimating the  $\left( \mathrm{O}_{\mathrm{X}_{\mathrm{CAPS}}}\right)_{\mathrm{error}}$  throughout the whole measurement period."

- Equation S3 assumes no error associated to the residence time. Is it correct to do so? What is the uncertainty associated to the residence time?

We did not include the error associated with the residence time in Equation 3. In a previous study (Hao et al., 2023), we assessed the error in residence time and determined it to be approximately 0.0007, with an average residence time of 0.063 h at a flow rate of 5 L min<sup>-1</sup>. Upon incorporating this residence time error into the calculation of  $P(O_3)_{net}$  error' using the 'error in the quotient' principle from the 'error propagation rules', we observed that the  $P(O_3)_{net}$  error' value decreased, with a reduction ranging from 0 to 2% [0.25-0.75 percentile]. This reduction is negligible compared to the  $P(O_3)_{net}$  error' calculated without accounting for the residence time error. Consequently, we chose not to consider the uncertainty related to the residence time in our calculations. We have provided this explanation in Supplement **S4. Measurement error of** *P***(O3)net and the LOD of the NPOPR detection system**:

"In our previous research (Hao et al., 2023), we evaluated the residence time error and determined it to be approximately 0.0007, with an average residence time of 0.063 hours at a flow rate of 5 L min<sup>-1</sup>. When we considered this error in the calculation of '*P*(O<sub>3</sub>)<sub>net</sub> error', we observed a minimal reduction in the ' $P(O_3)_{net}$  error' values, ranging from 0 to 2%  $[0.25-0.75$  percentile]. This impact is considered negligible in relation to the overall '*P*(O<sub>3)net</sub> error' as presented in Eq. (3). Consequently, we did not consider the uncertainty associated with the residence time in our calculations."

## 3/ Main paper

L205-207: "The measurement accuracy of NPOPR detection system is determined as 13.9 %, which is the maximum systematic error caused by the photochemical O3 productions in the reference chamber." – I do not understand this statement since the authors indicate on L214 that the measurement bias introduced by ozone production in the reference chamber is corrected for. The P(O3) measurement accuracy should therefore depend on the error associated with this correction. In addition, the measurement accuracy should account for other sources of errors such as the error associated to the residence time in the reaction and reference chambers.

Sorry for the confusing description. We agree with the reviewer that the  $P(O_3)_{net}$ corrections mentioned in lines 212-215 in the original manuscript, "Here, we employed the same modelling method described in Hao et al. (2013) to quantify the  $P(O_3)_{net}$  in the reference chamber and corrected the bias caused by the  $P(O_3)_{net}$  in reference chamber accordingly (more details can be found in Sect. 2.2.1)." are indeed related to the measurement accuracy of the NPOPR detection system as described in lines 206-208: "The measurement accuracy of the NPOPR detection system is determined as 13.9 %, representing the maximum systematic error resulting from photochemical  $O_3$  production in the reference chamber." We refer to this as the "accuracy of the NPOPR detection system" because it accounts for the systematic errors inherent in the system. These errors arise from photochemical  $O_3$ productions in the reference chamber, as a result of the UV protection Ultem film that only filters out the sunlight with wavelengths less than 390 nm. Consequently, photochemical O<sup>3</sup> production from sunlight wavelengths between 390 nm and 790 nm still exist in the reference chamber.

However, the error calculated in Eq. (S3) as described in Supplement **S4. Measurement error of** *P***(O3)net and the LOD of the NPOPR detection system** is considered as the measurement precision. This error refers to the degree of consistency or repeatability observed in a set of measurements by the NPOPR detection system. Here we have not taken in to account the uncertainty associated to the residence time, for the reasons outlined above.

### We have added this explanation in lines 199- 216 in the main text:

"The limit of detection (LOD) of the NPOPR detection system is 2.3 ppbv  $h^{-1}$  at the sampling air flow rate of 5 L min<sup>-1</sup>, which is obtained as three times the measurement error of  $P(O_3)_{net}$  (Hao et al., 2013). The measurement error of  $P(O_3)_{net}$  is determined by the estimation error of Ox in the reaction and reference chambers, which includes the measurement error associated with the  $O<sub>X</sub>$  of the CAPS-NO<sub>2</sub> monitor and the error due to the light-enhanced loss of  $O_3$ . This collective measurement error is referred to as the measurement precision of the NPOPR detection system, with further details provided in the supplementary materials, specifically in Sect. S4. The measurement accuracy of the NPOPR detection system is determined as 13.9 %, representing the maximum systematic error resulting from photochemical  $O<sub>3</sub>$  production in the reference chamber. Our earlier research indicated that the modelled  $P(O_3)_{net}$  in the reaction chamber is similar to that modelled in ambient air, with the modelled  $P(O_3)_{net}$  in the reference chamber accounting for 0-13.9% of that in the reaction chamber (Hao et al., 2023). This is due to the UV protection Ultem film covered on the reference chamber, which only filtered out the sunlight with wavelengths  $\leq$  390 nm, allowing photochemical  $O_3$  production **persist** at the sunlight wavelength between 390 nm and 790 nm. Here,

we have utilized the same modelling approach described in Hao et al. (2013) to quantify the  $P(O_3)_{net}$ in the reference chamber and corrected for the bias introduced by the measurement accuracy." And supplement S4:

"We note that this collective measurement error of  $P(O_3)_{net}$  is referred to as the measurement precision of the NPOPR detection system, which is different with the measurement accuracy of the NPOPR detection system described in Sect. 2.2.2."

Minor comments for the main paper:

L65-66: Shouldn't "while a VOCs-limited regime has lower VOCs/NOx ratios and the O3 formation is sensitive to NOx concentration changes" read "while a VOCs-limited regime has lower VOCs/NOx ratios and the O3 formation is sensitive to VOC concentration changes"?

Yes, it should be read 'while a "VOCs-limited" regime has lower VOCs/NOx ratios and the O<sub>3</sub> formation is sensitive to **VOCs** concentration changes.", we have corrected this sentence in the modified manuscript in lines 63-65.

L154: Please replace "self-developed" by "home-made"

Ok, we replaced "self-developed" by "home-made".

L184-185: It should be clearly stated that [Ox] concentrations plugged in Eq.1 are measured concentrations corrected from Ox losses in the reaction and reference chambers. Please replace "We further quantified and corrected the wall losses of Ox and the lightenhanced loss of O3 (d[O3]) in the reaction and reference chambers during daytime" by "[Ox] values plugged in Eq.1 to derive P(O3)net are measured values corrected for wall losses of Ox and the light-enhanced loss of O3 (d[O3]) in the reaction and reference chambers during daytime"

Thanks for pointing this out. We changed the sentence accordingly in lines 183- 185 in the modified manuscript.

L410: "5.1E-4" should read "5.1×10-4". Please also correct other instances of wrong formatting in the rest of the paragraph.

Ok, we corrected all instances of wrong formatting in the rest of the paragraph.

Figures 4 & 5: Please homogenize the notation between the main text and these figures d(O3) vs. d(Ox), R(O3) vs. R(Ox), P(O3) vs. P(Ox)

We homogenized the notation between the main text and Figs. 4 & 5 to  $d(O_X)/dt$ ,  $P(O_X)_{net}$ , and  $R(O_X)_{tran}$ .

L877-878: "The median value of the estimated error of the modelled P(O3)net ranged from 22-45 % during different episodes and non-episodes." Should read "The median relative difference between measured and modelled P(O3)net ranged from 22-45 % during different episodes and non-episodes."

# Thank you for the revision. We have corrected the sentence accordingly to make it clearer.

Minor comments for S3:

- "The light-enhanced loss coefficient of O3  $(y)$  was calculated using Eq. (4) described in the main text" should read "The light-enhanced loss coefficient of O3  $(y)$  was calculated using Eq. (2) described in the main text"

Sorry for this mistake. We corrected the sentence in S3 to "The light-enhanced loss coefficient of  $O_3(y)$  was calculated using Eq. (2) described in the main text".

## Appendix:

We detected other errors during the manuscript review and revised them as follows: In S3: we changed "The obtained  $\gamma$ -*J*(O<sup>1</sup>D) equation listed in Eq. (4) was used to correct for the light-enhanced loss of  $O_3$  in the reaction and reference chambers during the daytime to exclude the influence of light-enhanced loss." to "The obtained  $\gamma$ -*J*(O<sup>1</sup>D) equation listed in Fig. S8a was used to correct for the light-enhanced loss of  $O_3$  in the reaction and reference chambers during the daytime to exclude the influence of lightenhanced loss."

## References:

Hao, Y., Zhou, J., Zhou, J. P., Wang, Y., Yang, S., Huangfu, Y., Li, X. B., Zhang, C., Liu, A., Wu, Y., Zhou, Y., Yang, S., Peng, Y., Qi, J., He, X., Song, X., Chen, Y., Yuan, B., and Shao, M.: Measuring and modeling investigation of the net photochemical ozone production rate via an improved dual-channel reaction chamber technique, Atmos. Chem. Phys., 23, 9891-9910, 10.5194/acp-23-9891-2023, 2023.