

The manuscript of Zhou et al. reports novel information on the O<sub>3</sub> budget and chemistry at a monitoring site in the PRD region (China). This work takes advantage of ozone production rates measurements performed at the ground level during one month in Nov.-Dec. 2021 to infer the contributions of both photochemical and transport processes to the local ozone budget. In addition, the authors use a rich dataset of trace gas measurements performed at multiple heights (up to 335m) and 0-D box modeling to investigate the vertical distribution of P(O<sub>3</sub>). The ozone formation chemistry is investigated at the different heights, highlighting that ozone production occurs in the VOC-limited and transition regimes most of the time. The authors conclude that emission regulations focusing on the reduction of AVOCs and OVOCs should help reducing O<sub>3</sub> at this location.

We thank the reviewer's comments and suggestions, which will assist us in providing a more accurate description of our work. Our answers are listed in the following in red, after the reviewer's comments, which are in black. The modifications in the text are marked in yellow.

While the manuscript is well structured, the writing needs to be revised before publication. Some suggestions are provided below but there are more instances in the manuscript where improvements are needed. The methodology and the results seem scientifically sound and the authors provide novel information that will be of interest for the atmospheric community. I recommend publication after the authors have addressed the writing issues and the following comments:

Thanks to the reviewer's careful checking, we have revised the writing throughout the manuscript and changed the incorrect descriptions and grammar.

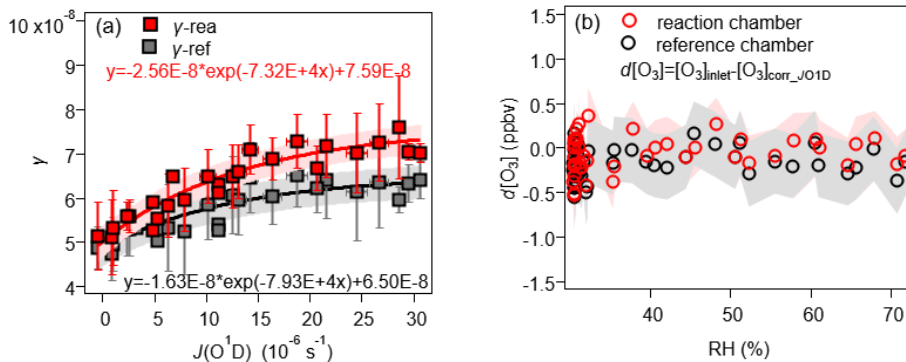
#### Major comments:

- L172-178: This section is confusing. The authors indicate that a light-enhanced loss of O<sub>3</sub> is corrected for but present an equation to compute an uptake coefficient for O<sub>3</sub>. It's not clear how the correction is done. The authors should clarify how this uptake coefficient is derived and how it is considered when computing  $P(O_3)_{net}$  from Eq. 1. The amplitude of this correction should also be clearly stated. It would be useful to add time series of  $P(O_3)_{net}$  with and without correction in the supplementary material to show how this correction changes over time.

We apologize for the unclear description. We have added the light-enhanced O<sub>3</sub> loss quantification method and the amplitude of this correction in the amended supplementary materials on page 9:

**S3. The experiments concerning the light-enhanced loss of O<sub>3</sub>**

*The light-enhanced loss of O<sub>3</sub> 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 experiment: the O<sub>3</sub> was injected at a mixing ratio of approximately 130 ppbv generated by the O<sub>3</sub> generator (P/N 97-0067-02, Analytic Jena US, USA) to ensure that no photochemical O<sub>3</sub> was produced during the outdoor experiment. The  $J(O^1D)$ ,  $T$ , RH,  $P$  and O<sub>3</sub> mixing ratios at the inlet and outlet of the reaction and reference chambers were measured simultaneously. The  $T$  and RH were measured with a thermometer (Vaisala, HMP110, USA). The light-enhanced loss coefficient of O<sub>3</sub> ( $\gamma$ ) was calculated using Eq. (4) described in the main text, and the relationship between  $J(O^1D)$  and  $\gamma$  is shown in Fig. S8a. The obtained  $\gamma$ - $J(O^1D)$  equation listed in Eq. (4) was used to correct for the light-enhanced loss of O<sub>3</sub> in the reaction and reference chambers during the daytime to exclude the influence of light-enhanced loss. The change in the O<sub>3</sub> mixing ratio after correcting for the light-enhanced loss of O<sub>3</sub> ( $d[O_3]$ ) showed no clear correlation with RH for both the reaction and reference chambers, as shown in Fig. S8b, indicating that the RH had no influence on the change in the O<sub>3</sub> mixing ratio during the observation period.



**Figure S8: The relationship between (a)  $\gamma$  and  $J(O^1D)$  and (b) RH and  $d[O_3]$  in the reaction and reference chambers, calculated from the 68.3 % confidence interval of the fit lines between  $\gamma$  and  $J(O^1D)$ , the shaded areas represent the maximum range of fluctuation under this confidence level.”**

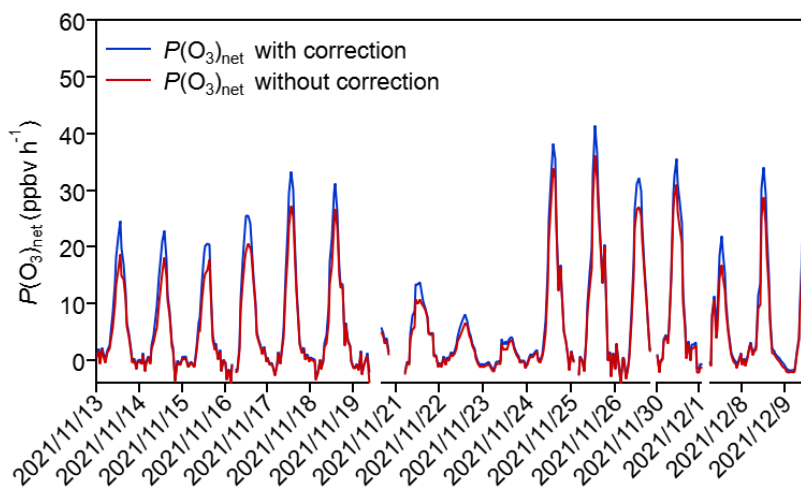
Accordingly, we have added the  $d[O_3]$  correction method on page 6-7, lines 188-198 in the revised manuscript:

“where  $\gamma$  is the light-enhanced loss coefficient of O<sub>3</sub>, which is derived from  $J(O^1D)$  according to the relationship obtained from the outdoor experiments (for more details, see supplementary materials: S3.).  $d[O_3]$  represents the difference between the O<sub>3</sub>

mixing ratios at the inlet and outlet of the reaction and reference chambers,  $D$  is the diameter of the chambers,  $\omega$  is the average velocity of  $O_3$  molecules,  $[O_3]$  is the injected  $O_3$  mixing ratio at the inlet of the reaction and reference chambers, and  $\tau$  is the average residence time of the air in the reaction and reference chambers. When quantifying the light-enhanced  $O_3$  loss ( $d[O_3]$ ) during the ambient air measurement, we first calculate  $\gamma$  using the measured  $J(O^1D)$  and the  $\gamma - J(O^1D)$  equations listed in Fig. S8 in the reaction and reference chambers, then use the measured  $[O_3]$  and Eq. 2 to calculate  $d[O_3]$ .

Furthermore, we quantified the amplitude of this correction by comparing the  $P(O_3)_{net}$  with and without the correction for the light-enhanced loss of  $O_3$ ; the corresponding time series are shown in Fig. S9 in the supplementary material to show how this correction changes with time:

“Furthermore, we quantified the light-enhanced loss of  $O_3$  correction by comparing the  $P(O_3)_{net}$  with and without the correction, the corresponding time series are shown in Fig. S9. Results show that such a correction can increase the measured  $P(O_3)_{net}$  by 10% (25% percentile) to 24% (75% percentile), with the median value of 17%.



**Figure S9: The time series of  $P(O_3)_{net}$  with and without the light-enhanced loss of  $O_3$  correction.**

The corresponding description is added on page 7, lines 198-199 in the modified manuscript:

“The results show that such kind of correction can increase the measured  $P(O_3)_{net}$  by 10% (25% percentile) to 24% (75% percentile), with a median of 17%.”

- L180-181: “The limit of detection (LOD) of the NPOPR detection system is 2.3 ppbv h<sup>-1</sup> at the sampling air flow rate of 5 L min<sup>-1</sup>,

which is obtained as three times the measurement error of  $P(O_3)_{net}$ .” – It’s not clear how the authors derive a LOD from the error associated to  $P(O_3)_{net}$ . This error will scale with  $P(O_3)_{net}$ . Please clarify.

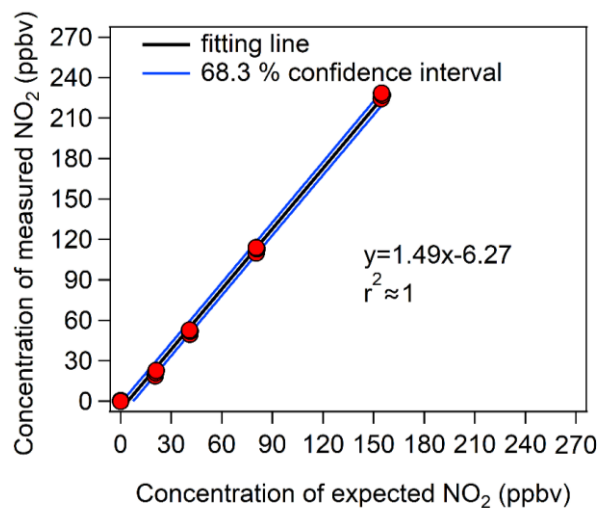
Ok, we have clarified the error associated with  $P(O_3)_{net}$  and described the derive method in detail in the supplementary material on pages 9-11:

**S4. Measurement error of  $P(O_3)_{net}$  and the LOD of the NPOPR detection system**

According to the  $P(O_3)_{net}$  evaluation method listed in Eq. (1) in the main text, the measurement error of  $P(O_3)_{net}$  depends on the estimation error of  $O_x$  in the reaction and reference chambers, which includes the measurement error of  $O_x$  of CAPS- $NO_2$  monitor and the error caused by  $\gamma$ , and can be calculated according to Eq. (S1) :

$$(O_x)_{error} = \sqrt{(O_{X\gamma})_{error}^2 + (O_{XCAPS})_{error}^2} \quad (S1)$$

where  $(O_{X\gamma})_{error}$  and  $(O_{XCAPS})_{error}$  represents the  $\gamma$  corrected error of the  $O_x$  of the reaction and reference chambers and the measurement error of the  $O_x$  of the CAPS- $NO_2$  monitor, respectively. The measurement error of the CAPS  $NO_2$  monitor was obtained by fitting the  $NO_2$  calibration results with a 68.3 % confidence level. The blue line in Fig. S10 represents the maximum range of fluctuation under this confidence level.



**Figure S10: Calibration results of the CAPS  $NO_2$  monitor at different  $NO_2$  mixing ratios. The y-axis represents the  $NO_2$  mixing ratios measured by the CAPS  $NO_2$  monitor, and the x-axis represents the prepared  $NO_2$  mixing ratios prepared from the diluted  $NO_2$  standard gas.**

$(O_{XCAPS})_{error}$  was then calculated from the fluctuation range of the 68.3 % confidence

interval of the calibration curve. The relationship between  $(O_{X_{CAPS}})_{error}$  and the measured  $O_x$  value ( $[O_x]_{measured}$ ) can be expressed as a power function curve, as shown in Eq. (S2):

$$(O_{X_{CAPS}})_{error} = 9.72 \times [O_x]_{measured}^{-1.0024} \quad (S2)$$

Dry pure air was sequentially introduced into the NPOPR detection system for ~ 2 h to adjust the system, followed by dry pure air or ambient air when the CAPS  $NO_2$  monitor time resolution was 1 s and the integration period was 100 s (the measurement durations for the reaction and reference chambers were both 2 min).

The measured  $O_x$  errors may also be influenced by the light-enhanced loss of  $O_3$  in the reaction and reference chambers under ambient conditions when the light intensity (especially  $J(O^1D)$ ) and  $O_3$  mixing ratios are high. Therefore, when injecting ambient air into the NPOPR system, the error of  $P(O_3)_{net}$  with a residence time of  $\tau$  can be calculated using Eq. (S3):

$$P(O_3)_{net\_error} = \sqrt{\frac{(O_{X_Y})_{rea\_error}^2 + ((9.72 \times [O_x]_{rea\_measured}^{-1.0024})_{rea\_std})^2 + (O_{X_Y})_{ref\_error}^2 + ((9.72 \times [O_x]_{ref\_measured}^{-1.0024})_{ref\_std})^2}{\tau}}$$

(S3)

where  $(O_{X_Y})_{rea\_error}$  and  $(O_{X_Y})_{ref\_error}$  represent the measurement error due to light-enhanced loss of  $O_3$  in the reaction and reference chambers, respectively, and  $((9.72 \times [O_x]_{measured}^{-1.0024})_{rea\_std})$  and  $((9.72 \times [O_x]_{measured}^{-1.0024})_{ref\_std})$  represent the standard deviation of  $O_x$  in the reaction and reference chambers, respectively, caused by the CAPS  $NO_2$  monitor with an integration time period of 100 s. Combined with the associated residence time  $\langle \tau \rangle$  under different flow rates, i.e.,  $\langle \tau \rangle$  was 0.063 h at a flow rate of  $5 \text{ L min}^{-1}$ .

The LOD of the NPOPR detection system was determined to be three times  $P(O_3)_{net\_error}$ . Since the measurement error of the CAPS  $NO_2$  monitor decreases with increasing  $O_x$  mixing ratios (as shown in Eq. S2), higher LODs could be obtained when injecting dry pure air into the NPOPR detection system, which were approximately 0.07, 1.4, and 2.3

ppbv h<sup>-1</sup> at air flow rates of 1.3, 3, and 5 L min<sup>-1</sup>, respectively. Given that the background O<sub>x</sub> mixing ratios (measured by the CAPS NO<sub>2</sub> monitor of the air in the reference chamber) changed when the ambient air was measured, the measured O<sub>x</sub> errors in the reaction and reference chambers changed with the O<sub>x</sub> mixing ratios, and the LOD must also be a function of the intrinsic ambient and photochemically formed O<sub>3</sub> and NO<sub>2</sub> mixing ratios (i.e., the O<sub>x</sub> mixing ratios measured by the CAPS NO<sub>2</sub> monitor).”

Accordingly, we have added the relevant description to the main text on pages 7, lines 202-205:

“More details about the measurement error of  $P(O_3)_{net}$  are described in the supplementary materials: S4: The measurement error of  $P(O_3)_{net}$  and the LOD of the NPOPR detection system. More details can be found in our previous work (Hao et al., 2013).”

- L194-195: “Therefore, we corrected the measured  $P(O_3)_{net}$  using the quantified  $P(O_3)_{net}$  in the reference chamber.” – How was  $P(O_3)_{net}$  quantified in the reference chamber?

We apologize for the confusing description. We quantified  $P(O_3)_{net}$  using the modelled values of  $P(O_3)_{net}$  in the reference chamber according to the method described in our previous study (Hao et al., 2023). We have added such descriptions in Sect. 2.2.2 (page 7, lines 210-216):

“According to our previous investigation, 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). 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).”

- L223-225: The authors should address the specificity of their NO<sub>2</sub> measurements since chemiluminescence instruments also detect some NO<sub>y</sub> species in the NO<sub>2</sub> channel. Were O<sub>3</sub>, NO and NO<sub>2</sub> corrected for O<sub>3</sub>+NO→NO<sub>2</sub> in the sampling line? If so, please indicate the amplitude of this correction.

Thanks for the suggestion. We used a commercially available chemiluminescence NO<sub>x</sub> monitor with the interference of HNO<sub>3</sub> and PANs on NO<sub>2</sub> measurement, and

compared the  $\text{NO}_2$  measured by the chemiluminescence  $\text{NO}_x$  monitor with that measured by the Cavity Attenuated Phase Shift (CAPS, which is considered to be a reliable  $\text{NO}_2$  measurement technique without chemical interference) and found that a 5% bias could be caused by the chemiluminescence  $\text{NO}_x$  monitor, which is shown in Zhou et al (2025). Therefore, we simulated  $P(\text{O}_3)_{\text{net}}$  by reducing and increasing the mixing ratios of  $\text{NO}_2$  by 5% to check the interference caused by using the chemiluminescence  $\text{NO}_x$  monitor to model  $P(\text{O}_3)_{\text{net}}$ . The results show that increasing and decreasing  $\text{NO}_2$  by 5% resulted in a decrease in  $P(\text{O}_3)_{\text{net}}$  of 1.64 % and 3.68 %, respectively, which is much smaller than the bias caused by  $P(\text{O}_3)_{\text{net}}$  in the reference chamber ( $\sim 13.9\%$ ), these tests are shown in Hao et al. (2023). However, this won't affect our measured  $P(\text{O}_3)_{\text{net}}$  values, as we used a CAPS  $\text{NO}_2$  monitor (Aerodyne research, Inc., Billerica MA, USA) in the net photochemical ozone production rate (NPOPR) detection system to avoid such interference, and quantified  $\text{O}_x$  ( $=\text{O}_3+\text{NO}_2$ ) differences in the reaction and reference chambers to correct for the effects of fresh  $\text{NO}$  titration to  $\text{O}_3$ . We have specified the interference of  $\text{NO}_2$  measurements using the chemiluminescence technique on pages 9, lines 263-269 in the amended manuscript:

“According to our test (Zhou et al., 2025), a 5% overestimation could be caused in the  $\text{NO}_2$  measurement using the chemiluminescence technique compared to the CAPS technique, due to some  $\text{NO}_z$  species (i.e.,  $\text{HNO}_3$ , peroxyacetyl nitrate (PANs),  $\text{HONO}$ , etc.)(Dunlea et al., 2007), this will result in a decrease of the modelled  $P(\text{O}_3)_{\text{net}}$  by  $< 4\%$ , which is negligible compared to the bias caused by the  $P(\text{O}_3)_{\text{net}}$  in the reference chamber ( $\sim 14\%$ ) (Zhou et al., 2023).”

And indicated the quantification method for  $\text{O}_3$  in the reaction and reference chamber on pages 6, lines 166-168 in the modified manuscript:

“To correct for the effect of fresh  $\text{NO}$  titration to  $\text{O}_3$ , we use  $\text{O}_x$  ( $=\text{O}_3+\text{NO}_2$ ) instead of  $\text{O}_3$  to quantify the  $\text{O}_3$  generated by photochemical reactions (Pan et al., 2015; Tan et al., 2018).”

- Section 2.2.3: The authors should provide some details about the GC measurements. It is stated that an offline GC was used. How were the VOCs sampled? How were the sampled analyzed? How and how often were calibration and zeroing done on the GC instrument?

OK, we have added more details about offline GC measurements on page 8, lines 243-256:

“For the off-line GC-MS-FID measurement, whole-air samples were collected using 3.2

L electro-polished stainless-steel canisters (Entech, USA) at 5 and 120 m at time intervals of two hours. Two automatic canister samplers connected to 12 canisters were used to collect the whole-air samples, with each of canister collecting the sample for 10 min. The canisters were analyzed within one week (Zhu et al., 2018). The concentrations of 56 NMHC species in the canister analyzed by GC-MS/FID were calibrated daily using the mixture of a photochemical assessment monitoring stations (PAMS) standard gas and pure N<sub>2</sub>. In addition, the mixture of PAMS standard gas and pure N<sub>2</sub> with species concentrations of 1 ppbv was injected into the analytical system every 10 samples to check the operational stability of the instrument. Pure N<sub>2</sub> was injected into the analytical system at the start and end of each day's analysis to provide reference blank measurements. A full list of all 56 non-methane hydrocarbons (NMHCs) can be found in the supplementary material (Table S2).”

- Section 2.3: The authors should add a subsection to explain how Ozone Formation Potential (OFP) values are computed. OFP values are reported in Table 1 and Figure 3, and discuss in the result section.

In dedeed. We have added “Sect. 2.3.5 O<sub>3</sub> formation potential” on pages 12, lines 351-357:

“The ozone formation potential is calculated using the product of the VOCs concentration and the maximum incremental reactivity (MIR) coefficient (dimensionless, gram of O<sub>3</sub> produced per gram of VOCs) (Carter et al., 2012):

$$OFP_i = \sum_i [VOC]_i \times MIR_i \quad (10)$$

Where  $OFP_i$  is the ozone formation potential of species  $i$ ,  $[VOC]_i$  is the mass concentration or emission of species  $i$ , and  $MIR_i$  denotes the maximum increment reactivity of species  $i$  (g O<sub>3</sub>/g VOCs).”

- Section 2.3.1: The authors should indicate which chemical species were constrained in the box model and how they were constrained. It is not clear how the authors deal with ozone in the model. In section 3.2.2, the authors compare simulated ozone concentrations to field observations, which seems to indicate that measured ozone concentrations were not



directly constrained in the model. However, if the O<sub>3</sub> advected to the site was not constrained, the simulations would very likely not reproduce the measured ozone concentrations. How did the authors constrain the ozone transported to the observation site in their model?

Yes, we did not constrain the O<sub>3</sub> concentrations in our model, nor the O<sub>3</sub> advected to the site. We used a constant dilution factor of 1/432000 s<sup>-1</sup> throughout the modeling period and a sedimentation factor of 0.42 cm s<sup>-1</sup> for the physical processes of O<sub>3</sub>. We also added an O<sub>3</sub> background of 30 ppbv to represent the ozone transported to the observation site. We added the detailed chemical species constrained method in Sect. 2.3.1:

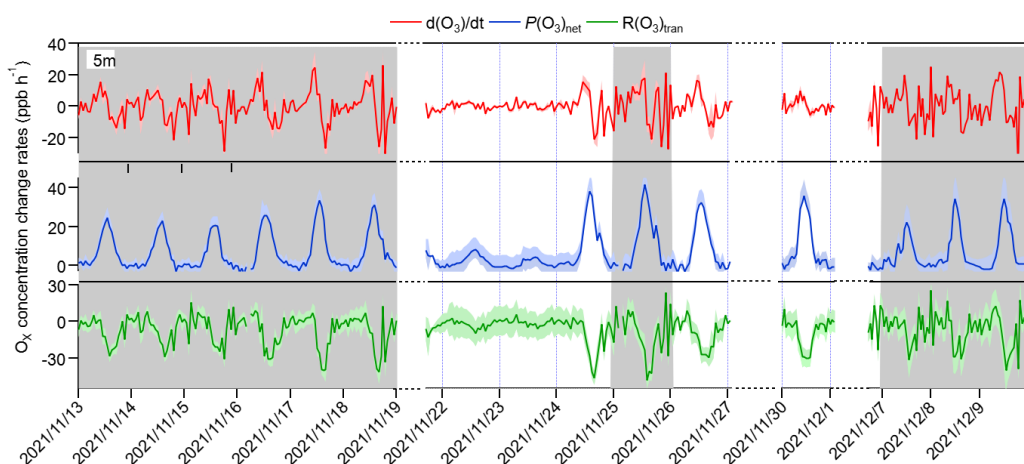
“ $P(O_3)_{net}$  and O<sub>3</sub> concentrations were simulated by constraining  $T$ , RH,  $P$ , organic and inorganic substances in gases, including 12 OVOCs (methanol, ethanol, formaldehyde, acetaldehyde, acrolein, acetone, hydroxyacetone, phenol, *m*-cresol, methyl vinyl ketone, methacrylaldehyde, methyl ethyl ketone), 56 NMHCs (toluene, benzene, isoprene, styrene, etc. as listed in Table S2), conventional pollutants (O<sub>3</sub>, NO, NO<sub>2</sub>, and CO), and photolysis rate values ( $J(O^1D)$ ,  $J(NO_2)$ ,  $J(H_2O_2)$ ,  $J(HONO)$ ,  $J(HCHO\_M)$ ,  $J(HCHO\_R)$ ,  $J(NO_3\_M)$ ,  $J(NO_3\_R)$ , etc.). The VOCs, NO<sub>x</sub>,  $T$ , RH and  $P$  were constrained throughout the modelling period, while O<sub>3</sub> was not constrained after providing initial concentration values. The effect of physical processes (such as vertical and horizontal transport) was considered by setting a constant dilution factor of 1/432000 s<sup>-1</sup> throughout the modelling period. Additionally, the dry deposition rate of O<sub>3</sub> was set to 0.42 cm s<sup>-1</sup>, and the background of O<sub>3</sub>, CO, and CH<sub>4</sub> were set to 30, 70, and 1800 ppbv, respectively. The modelling was run in a time-dependent mode with a resolution of 5 min, and it was run for spin-up time of 72 h to establish steady-state concentrations for secondary pollutants that were not constrained during the simulation.”

- Figure 4: The authors should indicate how R(O<sub>3</sub>)<sub>tran</sub> is derived. Is it computed as  $d[O_3]/dt - P(O_3)_{net}$ ? Please add error bars on the time series of  $d[O_3]/dt$ ,  $P(O_3)_{net}$  and R(O<sub>3</sub>)<sub>tran</sub>.

Yes, the  $R(O_3)_{trans}$  is computed as  $\frac{dO_x}{dt}$  minus  $P(O_x)_{net}$ , we have added how  $R(O_3)_{trans}$  is derived on page 19-20, lines 531-535 in the revised manuscript:

“ $R(O_x)_{trans}$  at 5 m ground level was derived from  $\frac{dO_x}{dt}$  minus  $P(O_x)_{net}$  according to Eq. (5) shown Sect. 2.3.2, their hourly averages and diurnal variations are shown in Figs. 4 and 5, respectively. From these figures, it is evident that the fluctuation of the  $O_3$  concentration change rate ( $d(O_3)/dt$ ) at ground level is typically small and primarily dominated by the physical processes during nighttime.”

We have added the error bars to the time series of  $d[O_3]/dt$ ,  $P(O_3)_{net}$  and  $R(O_3)_{tran}$  in Fig. 4:



**Figure 4. Time series of  $O_3$  concentration changes ( $d(O_3)/dt$ ) and contributions from local photochemical production ( $P(O_3)_{net}$ ) and physical transport ( $R(O_3)_{tran}$ ). The shaded areas of  $d(O_3)/dt$ ,  $P(O_3)_{net}$ , and  $R(O_3)_{tran}$  represent one standard deviation (denoted by  $\sigma$ ) of the mean  $d(O_3)/dt$ , the uncertainty of measured  $P(O_3)_{net}$ , and the propagated error of  $R(O_3)_{tran}$ , respectively.**

- L535: Dilution was constrained in the model using a species lifetime of 12h. How sensitive are the simulation results to this parameter? Please indicate how modelled  $P(O_3)$  changes when the lifetime is varied from 6 to 24 h. How does it affect the main conclusions?

To achieve the best agreement between the modelled  $O_3$  concentrations and the observed values, we applied different dilution factors (the species lifetime) in the modelling, which varying from 6 h to 24 h. We found that the simulated  $O_3$  is closest to the measured  $O_3$  concentrations when we set the species lifetime to 12 h. We found that the modelled  $P(O_3)_{net}$  increases with increasing dilution factor, but this doesn't affect our main conclusions as the influence of the dilution factor on the modelled  $P(O_3)_{net}$  is negligible due to the very short lifetime of the  $HO_2$  and  $RO_2$  radicals that determine the  $P(O_3)_{net}$  values.

According to our previous study, a 50 % change in the physical loss lifetime results in only 3 %, 6 % and 10 % changes in OH concentration, HO<sub>2</sub> concentration and ozone production rate, respectively (Wang et al., 2021). We have added the discussion in the main text on page 21-22, lines 598-607:

“To achieve the best agreement between the modelled O<sub>3</sub> concentrations and the observed values, we applied different dilution factors (the lifetime of the species) in the modelling, varying from 6 h to 24 h. We found that the simulated O<sub>3</sub> is closest to the measured O<sub>3</sub> concentrations when the lifetime of the species is set to 12 h. The modelled  $P(O_3)_{net}$  increases with the decrease of the dilution factor, but this doesn't affect the main conclusions as the influence of the dilution factor on the modelled  $P(O_3)_{net}$  is negligible due to the very short lifetime of the HO<sub>2</sub> and RO<sub>2</sub> radicals that determine the  $P(O_3)_{net}$  values (Wang et al., 2021). Therefore, a constant dilution factor of 1/43200 s<sup>-1</sup> was set throughout the observation period.”

- L541-543: Some values are provided for NMB and NME without addressing what it means for the model performance. The authors should comment these values in the text.

We have addressed the meaning of NMB and NME in the revised modified manuscript on page 22, lines 614-617:

“These analysis results indicate that the model underestimates the measured  $P(O_3)_{net}$  by a factor ranging from 1.42 (25<sup>th</sup> percentile) to 1.31 (75<sup>th</sup> percentile), calculated as  $(1+|NMB|)$ , and the simulation results are reliable (with  $-1 < NME < 1$ ).”

#### Minor comments:

- L68-71: The authors should provide a brief summary of what is known about ozone formation in the PRD region.

Ok, we have made a brief summary of what is known about ozone formation in the PRD area on page 3, lines 72-77:

“Currently, many scholars have analyzed the relationship between tropospheric ozone pollution and its precursors and meteorological elements in the PRD region, results show that the surface O<sub>3</sub> pollution is determined by both local photochemistry and physical transport, with long-range transport contributing 30%-70% to surface O<sub>3</sub> concentrations (Mao et al., 2022; Shen et al., 2021; Li et al., 2012, 2013).”

We have replaced the reference of (Li et al., 2022a) with (Mao et al., 2022; Shen et al., 2022; Li et al., 2012, 2013) to properly support our findings.

- L121-122: What is the air residence time in the sampling lines?

The residence time of the sample gas is inversely proportional to the flow rate and the tube length. In our study, the tube length ranged from 5 m (at 5 m height) to 400 m (at 335 m height). At a tube length of 400 m, the residence time is less than 180 s at a flow rate of 13 SLPM. We have added a corresponding description on page 5, lines 142-145:

“Consequently, the flow rates of the air sample streams for the six tubes varied between 12.0 and 15.0 SLPM without subsampling and were less than 20 SLPM with subsampling. The residence time of the sample gas in the longest tube (~ 400 m) is less than 180 s at a flow rate of 13 SLPM.”

- L158-168: This section is not necessary here. Please just indicate that pulse experiments were performed to quantify the residence time in the chambers and cite the paper of Hao et al. (2023).

Ok, we deleted the very detailed method for quantifying residence time and changed the related description of it on page 6, lines 181-183:

“A schematic of the NPOPR detection system is shown in Fig. S2. The pulse experiments were performed to quantify the residence time in the chambers (Hao et al., 2023).”

- L208-210: Please indicate the frequency and duration of zero measurements.

Ok, we have added the frequency and duration of zero measurements on page 8, lines 229-230:

“The background signal of each mode was measured every 30 min for at least 2 min by automatically switching the ambient measurement to a custom-built platinum catalytic converter heated to 365 °C.”

- L212: Please provide the E/N value.

Ok, we have provided the E/N value on page 8, lines 232-235 in the modified manuscript:

“Eventually, we only used VOCs measured during the  $\text{H}_3\text{O}^+$  mode, which was operated at a drift tube pressure of 3.8 mbar, a temperature of 120 °C, and a voltage of 760 V, resulting in an  $E/N$  ( $E$  refers to the electric field and  $N$  refers to the number density of the buffer gas in the drift tube) value of  $\sim 120$  Td (townsend).”

- L233: “the photolysis of  $\text{NO}_2$  at 424 nm” – please provide a range of wavelength instead of a unique wavelength.

Sorry for this mistake, thanks for pointing this out. The photolysis wavelength of  $\text{NO}_2$  should be less than 420 nm. We have changed the description on page 9, line 274-276 in the revised manuscript:

“The specific tropospheric  $\text{O}_3$  photochemical formation process involves the photolysis of  $\text{NO}_2$  at  $< 420$  nm (Sadanaga et al., 2017).”

- L550: Please remove “and in Indiana in the United States ( $\sim 30$  ppbv h<sup>-1</sup> in spring) (Sklaveniti et al., 2018)”. Sklaveniti et al. did not measure ambient  $\text{P}(\text{O}_3)$  but investigated the sensitivity of  $\text{P}(\text{O}_3)$  to  $\text{NO}$  additions in the instrument.

We apologize for this mistake. We have checked the paper again and removed this sentence accordingly.

- L570: Please rephrase. It’s not clear what is meant by “underestimate the  $\text{NO}_x$  limited regime”

We apologize for the confusing description. We meant that the underestimation of the modelled  $\text{P}(\text{O}_3)_{\text{net}}$  due to the unknown mechanisms could lead to the  $\text{NO}_x$ -limited regime being shifted to the VOCs-limited regime, as illustrated in Wang et al. (2022, 2024), thus underestimating the  $\text{NO}_x$  regime. We have changed the description on pages 23, lines 639-647 in the revised manuscript.

“For example, the reaction of OH with unknown VOCs (Tan et al., 2017), the lack of correction for the decomposition of  $\text{CH}_3\text{O}_2\text{NO}_2$ , the missing  $\text{RO}_2$  production from photolysis  $\text{ClNO}_2$  (Whalley et al., 2018; Tan et al., 2017), and the underestimation of OVOCs photolysis (Wang et al., 2022) in modelling approaches may lead to the underestimation of  $\text{RO}_2$ , thus underestimating the modelled  $\text{P}(\text{O}_3)_{\text{net}}$ . Further analysis showed that the underestimation of  $\text{P}(\text{O}_3)_{\text{net}}$  can lead to the  $\text{NO}_x$ -limited regime being

shifted to the VOCs-limited regime, thus underestimating the NO<sub>x</sub>-limited regime (Wang et al., 2022, 2024).”

- L793-794: “The maximum estimated error of modelled  $P(O_3)_{net}$  ranged from 22-45 % during different episodes and non-episodes.”. This has not been discussed in the manuscript before the general conclusion. The authors should discuss this point in more details the manuscript. How is the 22-45% error estimated?

We apologize for the lack of discussion of this in the manuscript before the general conclusion. The 22-45% error was estimated as the median of the modelled  $P(O_3)_{net}$  bias, i.e., the median value of  $[measured P(O_3)_{net}-modelled P(O_3)_{net}]/measured P(O_3)_{net}$  during different episodes and non-episodes. We have added the related discussion in the main text on page 23, lines 632-634:

“The median value of  $[measured P(O_3)_{net}-modelled P(O_3)_{net}]/measured P(O_3)_{net}$  ranged from 22% to 45% for different episodes and non-episodes.”

And changed the related description on page 31, lines 875-877:

“The median value of the estimated error of the modelled  $P(O_3)_{net}$  ranged from 22-45 % during different episodes and non-episodes.”

- L32: “photochemical reactions play a dominate role” should read “photochemical reactions playing a major role”

We have changed this description accordingly on page 1-2, lines 30-32:

“The identified O<sub>3</sub> pollution episodes were found to be jointly influenced by both photochemical production and physical transport, with local photochemical reactions playing a major role.”

- L56: “Tropospheric ozone (O<sub>3</sub>), which have adverse effects on ecosystems” should read “Tropospheric ozone (O<sub>3</sub>), which has adverse effects on ecosystems”

We have modified the description on page 2, line 56:

“Tropospheric ozone (O<sub>3</sub>), which has adverse effects on ecosystems, climate change, and human health (Fiore et al., 2009; Anenberg Susan et al., 2012; Seinfeld, 2016),...”

- L58: “important factor resulting severe regional air pollution” should read “important factor resulting in severe regional air pollution”

We apologize for this mistake. We have modified this sentence on page 2, lines 58:

“Tropospheric ozone (O<sub>3</sub>), which has adverse effects on ecosystems, climate change, and human health (Fiore et al., 2009; Anenberg Susan et al., 2012; Seinfeld, 2016), have become an important factor resulting in severe regional air pollution in China (Zhu et al., 2020).”

- L59: “Tropospheric O<sub>3</sub> mainly comes from the external transport from the stratosphere” should read “Tropospheric O<sub>3</sub> mainly comes from stratospheric intrusions”

We have modified the description on page 2, lines 59:

“Tropospheric O<sub>3</sub> mainly comes from stratospheric intrusions and the photochemical reactions of O<sub>3</sub> precursors, involving volatile organic compounds (VOCs) and nitrogen oxides (NO<sub>x</sub>=NO+NO<sub>2</sub>),”

- L87-88: “thus largely hindered our in depth understanding of” should read “thus largely hindering our understanding of”

We have changed the description on page 3-4, lines 96-100:

“Owing to the low time resolution of these monitoring techniques, achieving continuous vertical coverage of VOCs and NO<sub>x</sub> measurements is challenging. Consequently, the vertical distribution structure of VOCs remains unclear, thus largely hindering our understanding of the vertical and temporal regional ozone formation mechanism.”

- L90: “observation system based on the Shenzhen Meteorological Gradient Tower” should read “observation system located on the Shenzhen Meteorological Gradient Tower”

We actually meant that the vertical observation system was built based on the basis of the Shenzhen Meteorological Gradient Tower (SZMGT). We have changed this sentence on page 4, lines 101-103:

“To fill the gaps in the existing studies, we utilized a newly constructed vertical observation system based on the Shenzhen Meteorological Gradient Tower (SZMGT) (Li et al., 2023).”

- L92: “To diagnose the  $P(O_3)_{net}$  and  $O_3$  formation” should read “To diagnose the net ozone production rate,  $P(O_3)_{net}$ , and  $O_3$  formation”

We have changed this sentence on page 4, lines 104:

“To diagnose the net ozone production rate,  $P(O_3)_{net}$ , and  $O_3$  formation sensitivities across various heights,”

- L94: “with the Master Chemical Mechanism (MCM v3.3.1).” should read “with the Master Chemical Mechanism (MCM v3.3.1), referred to as OBM-MCM in the following.”

We have changed this description on page 4, lines 105-107:

“we employed an observation-based model coupled with the Master Chemical Mechanism (MCM v3.3.1), referred to as OBM-MCM in the following.”

- L104: “while acknowledging potential biases associated modelling.” Should read “while acknowledging potential biases associated to the modelling.”

We have changed this sentence on page 4, lines 114-116:

“we have extensively discussed the vertical and temporal variability in  $P(O_3)_{net}$  and  $O_3$  formation sensitivity, while acknowledging potential biases associated to the modelling.”

- L172: “[ $O_3$ ] represents the difference should read “ $d[O_3]$  represents the difference”

We have changed the description on page 6, lines 190:

“ $d[O_3]$  represents the difference between the  $O_3$  mixing ratios at the inlet and outlet of the reaction and reference chambers”

- L 173 & L184: “(Hao et al., 2013) » should read “(Hao et al., 2023).”



We apologize for this mistake. We have changed it to “(Hao et al., 2023).”

- L198: “mass spectrometry » should read « mass spectrometer”

We have changed it on page 7, lines 219:

“VOCs were measured using a high-resolution proton transfer reaction time-of-flight mass spectrometer (PTR-TOF-MS, Ionicon Analytik, Austria) (Wang et al., 2020a; Wu et al., 2020) and an off-line gas chromatography mass spectrometry flame ionization detector (GC-MS-FID) (Wuhan Tianlong, Co. Ltd, China) (Yuan et al., 2012).”

- L241-247: Please rephrase. This sentence does not have a conjugated verb.

We apologize for this mistake. We rephrased this sentence accordingly on page 9, lines 284-285:

“ $P(O_3)_{net}$  and  $O_3$  concentrations were simulated by constraining  $T$ , RH,  $P$ , organic and inorganic substances in gases, including...”

- L268: “ $P(O_3)_{net}$  denotes the net photochemical  $O_3$  production rate (ppbv h<sup>-1</sup>)” should read “ $P(O_x)_{net}$  denotes the net photochemical  $O_3$  production rate (ppbv h<sup>-1</sup>)”

We have changed this sentence on page 11, line 319:

“Where  $\frac{dO_x}{dt}$  is the change rate of the observed  $O_x$  mixing ratio change (ppbv h<sup>-1</sup>),  $P(O_x)_{net}$  denotes the net photochemical  $O_3$  production rate (ppbv h<sup>-1</sup>), which was equal to  $P(O_3)_{net}$  and measured directly by the NPOPR system,  $R(O_x)_{trans}$  represents  $O_3$  mixing ratio change due to the physical transport (ppbv h<sup>-1</sup>), including the horizontal and vertical transport, dry deposition and the atmospheric mixing (Liu et al., 2022).”

- L297: “different kinds of VOCs groups together to investigated their influence to the gradient  $P(O_3)_{net}$  change with heights in Sect. 3.2.3.” should read “different kinds of VOC groups together to investigate their influence on the vertical gradient of  $P(O_3)_{net}$  in Sect. 3.2.3.”

We have changed the description on page 11, lines 347-349:

“In this study, we summarized the OH reactivities of different kinds of VOCs groups together to investigate their influence on the vertical gradient  $P(O_3)_{net}$  in Sect. 3.2.3.”

- L454: “As concluded in Sect. 3.3.1” should read “As concluded in Sect. 3.1.1”

We have changed the description on page 18, lines 508:

“As concluded in Sect. 3.1.1 O<sub>3</sub> pollution episodes may be jointly affected by the photochemical reactions and physical transport.”

- L458: “As the dry deposition are usually contribute” should read “As dry deposition usually contributes”

We have changed the sentence on page 17, lines 512-514:

“Typically, as dry deposition contributes a relatively small portion and can often be considered negligible, making vertical and horizontal transport the main contributors to physical processes (Tan et al., 2019).”

- Legend Figure 5: “R(O<sub>3</sub>)net” should read “R(O<sub>3</sub>)tran”

We have changed the legend of “R(O<sub>3</sub>)net” to “R(O<sub>3</sub>)trans” in Fig. 5.

- L504: “concentration became stable, suggests that the photochemical reaction competed against physical transport and jointly affect O<sub>3</sub> concentration change” should read “concentration became stable, suggesting that the photochemical reaction competed against physical transport and jointly affected O<sub>3</sub> concentration change”

We have changed this sentence on page 21, lines 570:

“Around noon, O<sub>3</sub> concentrations stabilize, suggesting a balance between photochemical reactions and physical transport affecting O<sub>3</sub> concentration changes.”

- L 506: “the O<sub>3</sub> concentration decreases due to the diffuse of photochemically formed O<sub>3</sub>” should read “the O<sub>3</sub> concentration decreases due to the transport of photochemically formed O<sub>3</sub>”

We modified the description on page 21, lines 571-573:

“O<sub>3</sub> concentration decreases due to the transport of photochemically formed O<sub>3</sub> from the observation site to upward directions or the surrounding areas.”

- L514: “with O<sub>3</sub> diffuse to » should read “with O<sub>3</sub> transport to”

We modified the description on page 21, lines 580:

“②elevated photochemical O<sub>3</sub> production, with O<sub>3</sub> transport to surrounding areas under favorable diffusion conditions (i.e., non-episodes II).”

- L558: “presence of missing RO<sub>2</sub> under high NO conditions” should read “underestimation of RO<sub>2</sub> under high NO conditions”

We modified this sentence on page 22-23, lines 628-632:

“The measured  $P(O_3)_{net}$  were mostly higher than the modelled  $P(O_3)_{net}$ , which could be attributed to the underestimation of RO<sub>2</sub> under high NO conditions, leading to substantial disparities between calculated  $P(O_3)_{net}$  derived from measured and modelled RO<sub>2</sub> concentrations, as highlighted in previous studies (Whalley et al., 2018, 2021; Tan et al., 2017, 2018).”

- L569-570: “OVOCs photolysis (Wang et al., 2022) in modelling approach, may result in the underestimation of RO<sub>2</sub>, thus underestimate the modelled  $P(O_3)_{net}$ ” should read “OVOCs photolysis (Wang et al., 2022) in modelling approaches, may result in the underestimation of RO<sub>2</sub>, thus underestimating the modelled  $P(O_3)_{net}$ ”

We modified the sentence on page 23, lines 639-644:

“For example, the reaction of OH with unknown VOCs (Tan et al., 2017), the lack of correction for the decomposition of CH<sub>3</sub>O<sub>2</sub>NO<sub>2</sub>, the missing RO<sub>2</sub> production from photolysis ClNO<sub>2</sub> (Whalley et al., 2018; Tan et al., 2017), and the underestimation of OVOCs photolysis (Wang et al., 2022) in modelling approaches may lead to the underestimation of RO<sub>2</sub>, thus underestimating the modelled  $P(O_3)_{net}$ .”

- L700: “heights, indicates the similar photochemical O<sub>3</sub> formation regime” should read “heights, indicating a similar photochemical O<sub>3</sub> formation regime”

We modified the sentence on page 27, lines 769-771:

“As illustrated in Fig. 9, the RIR values for different O<sub>3</sub>-precursors or precursor groups don’t exhibit significant variation at different heights during specific episodes or non-episodes, indicating a similar photochemical O<sub>3</sub> formation regime.”

- L708: “during polluted episode I, both reduce VOCs and NOx” should read “during polluted episode I, reducing both VOCs and NOx”

We modified the sentence on page 27-28, lines 778-779:

“For example, during polluted episode I, reducing both VOCs and NOx can mitigate photochemical O<sub>3</sub> formation, but during the other O<sub>3</sub> polluted episodes and non-episodes, reduce VOCs can effectively alleviate photochemical O<sub>3</sub> formation, while the reduction of NOx might aggravate photochemical O<sub>3</sub> formation.”

- L724: “which located in the » should read “which is located in the”

We modified the description on page 28-29, lines 807-809:

“This suggests a transition in the photochemical O<sub>3</sub> formation regime throughout the day, shifting from a VOC-limited regime in the morning to a transition regime and more sensitive to NOx in the afternoon around 16:00 LT.”

- L731: “ROx radicals cycle reactions involved Nox” should read “ROx radicals cycle reactions involving NOx”

We modified the description on page 29, lines 814:

“Through the sensitivity study, NOx is not found to be the limiting factor affecting  $P(O_3)_{net}$ , therefore, reactions involving NOx in the ROx radicals cycle, such as  $RO_2+NO \rightarrow HO_2$  and  $HO_2+NO \rightarrow OH$ , should occurred efficiently.”

- L754: “Given that NOx has a significant titration effect on ozone” should read “Given that NO has a significant titration effect on ozone”

We modified the sentence on page 29, lines 837:

“Given that NO has a significant titration effect on ozone, the lower O<sub>3</sub> concentration at ground level may be attributed to the increase in NOx concentration due to a more pronounced NO titration effect, besides the dry deposition near the ground.”

- L766: “with local photochemical reactions play a dominate role” should read “with local photochemical reactions playing a key role”

We modified the sentence accordingly on page 30, lines 849-850:

“we found that the O<sub>3</sub> pollution episodes were jointly influenced by both photochemical production and physical transport, with local photochemical reactions playing a key role.”

- L771: “the measurement period, indicated the” should read “the measurement period, indicating the”

We modified it accordingly on page 30, lines 854-855:

“The index of agreement (IOA) ranged from 0.87 (25<sup>th</sup> percentile) to 0.90 (75<sup>th</sup> percentile) for the measured and modelled  $P(O_3)_{net}$  across the measurement period, indicating the rationality to investigate the vertical and temporal variability of O<sub>3</sub> formation mechanism using modelling results.”

- L774: “differences of measured and modelled  $P(O_3)_{net}$ ” should read “differences between measured and modelled  $P(O_3)_{net}$ ”

We modified the sentence on page 30, lines 856-858:

“However, the measured  $P(O_3)_{net}$  generally exceeded the modelled  $P(O_3)_{net}$ , the differences between measured and modelled  $P(O_3)_{net}$  ( $\Delta P(O_3)_{net}$ ) were found to be correlated with NO concentrations.”

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