We would like to thank the referee for their recheck and valuable feedbacks, which further improved the quality of the paper. We have addressed the comments point-by-point. The reviewer's comments are in black, our answers are reported in red, and the modifications we made in the manuscript are highlighted in yellow.

## Reviewer #2

General Comments:

This manuscript details changes made to a two-chamber system used to directly measure ambient net ozone production rates, sensitivity tests conducted on this system, and a final 0-D box modeling comparison of the chemistry in both chambers and in ambient air for a select measurement day in 2021. The criticality of making such direct  $P(O_3)_{net}$  measurements in areas with poor air quality for the purpose of determining efficient  $O_3$  mitigation strategies is not refuted here; this is an important issue globally. However, while it is clear that much work has gone into the manuscript, it requires major revisions both scientifically and grammatically before being referred for publication. Given the nature of the manuscript, I wonder whether submission to Atmospheric Measurement Techniques is more suitable.

Thanks for the reviewer's insightful comments. As the  $P(O_3)_{net}$  measurement system was built based on the dual-channel reaction chamber technique promoted by previous studies, we mainly described how to extend this technique to variable environments by making some improvements and then applied it to a typical  $O_3$ polluted area in China to investigate the photochemical  $O_3$  formation mechanism. This is the first time we have used the direct  $P(O_3)_{net}$  measurement technique in China, and the results extended previous modeling studies and can be used for comparison with our current knowledge. Therefore, we assume that this manuscript is more relevant to the application of such a technique in mechanism exploration than the measurement technique itself; thus, we think its content is relevant to the scope of Atmospheric Chemistry and Physics and will be of interest to its readership. According to the reviewer's suggestions, we have reorganized the manuscript and revised the manuscript scientifically and grammatically.

## Specific Comments:

In general, the manuscript is structured appropriately, but has a number of grammatical errors within that prevent clear and fluent presentation. The manuscript would benefit from a review by a technical editor. Some suggestions are presented in the technical corrections below.

Thank you for the reviewer's corrections. we have modified the suggestions pointby-point and then asked a technical editor to review our manuscript to make the description more clearly and fluently. Equation (1), the ambient  $O_3$  budget, is also dependent upon entrainment from the stratosphere. Please add this term for completeness.

Indeed. We added the  $O_3$  entrainment from the stratosphere in  $O_3$  budget in the modified manuscript in page 3, lines 53-62.

The manuscript indicates that the same tests were conducted on the NPOPR system as in other studies (L188-L189). However, several sensitivity tests conducted in previous studies (Sklaveniti et al., 2018; Baier et al., 2017) are missing from this analysis. These include the following: biases on  $P(O_3)_{net}$  from temperature differences between the reaction and reference chamber; short-duration baseline drifting in the CAPS monitor (in presence of both dried and humidified air) and HONO production. Given that some of these additional tests have not been conducted, it is difficult to assess whether the NPOPR system described here has significant improvements over other systems described in the literature. Further, a more detailed description of the system, materials used, switching for sample analysis, etc. would be helpful for characterizing potential differences between this chamber system and others described in previous literature.

Thanks for pointing these out. We have carefully checked the sensitivity tests conducted in previous studies (Sklaveniti et al., 2018; Baier et al., 2017), and conducted some additional tests, the responses for all the points mentioned above are listed as follows:

(1) biases on  $P(O_3)_{net}$  from temperature differences between the reaction and reference chamber:

The only difference between the reaction and reference chambers in the NPOPR detection system described here is that the reference chamber was covered by a UV protection Ultem film (SH2CLAR, 3 M, Japan) to block sunlight with wavelengths < 390 nm. This type of film was supposed to not block the heat outside the reference chamber, thus preventing a temperature difference between the two chambers. We measured the temperature both in the reaction and reference chambers when running the NPOPR system in an ambient observation during November 2022 on the Panyu campus of Jinan University in Guangzhou, China (113° 36' E, 23° 02' N). We found that the temperature remained the same in both chambers during the measurement period, as shown in Fig. S10.



Figure S10. Air temperature in the reaction and reference chambers during the ambient field observation on Panyu campus of Jinan University.

Accordingly, we added this test in the main manuscript in page 9, lines 200-203:

"We characterized the NPOPR detection system following the same procedures as previous researchers, including the residence time of the air, the wall losses of NO<sub>2</sub> and O<sub>3</sub>, the transmittance of light and temperature differences in the reaction and reference chambers, and the quantitative conversion efficiency of O<sub>3</sub> to NO<sub>2</sub> ( $\alpha$ ) in the NO-reaction chamber."

and in page 10, lines 234:

"The light transmittance <mark>and temperature differences in the reaction and reference chambers.</mark>"

and in pages 11-12, line 265-270:

"We further detected the temperature in both the reaction and reference chambers when running the NPOPR system in an ambient observation campaign during November 2022 on the Panyu campus of Jinan University in Guangzhou, China (113° 36′ E, 23° 02′ N). We found that the UV protection Ultern film on the reference chamber did not block the heat outside the chamber, and the temperature remained the same in the reaction and reference chambers during the measurement test, as shown in Fig. S10."

(2) short-duration baseline drifting in the CAPS monitor (in presence of both dried and humidified air):

We added the tests for the baseline drift of CAPS at different humidities. As shown in Fig. S11, the CAPS baseline did not shift significantly as the humidify changed:

(a) when injecting ambient air to CAPS, the baseline drifts were 0.035 and 0.032 ppbv (1  $\sigma$ ) at an integration time of 35 and 100 s, respectively; (b) when injecting wet pure air to CAPS, the baseline drifts were 0.043 and 0.030 ppbv (1  $\sigma$ ) at an integration time of 35 and 100 s, respectively; (c) when injecting dry pure air to CAPS, the baseline drifts were 0.043 and 0.047 ppbv at an integration time of 35 and 100 s, respectively. Thus, we chose the biggest baseline drift when injecting dry pure air to estimate the  $P(O_3)_{net}$  error and calculate the limit of detection of CAPS (which were 0.13 and 0.14 ppbv (3  $\sigma$ ) at an integration time of 35 and 100 s, respectively, as shown in Sect. 2.3). By doing this, we were able to include all the short-duration baseline drifting in the CAPS monitor under different humidities. Accordingly, we modified the description in page 15, lines 343-357 in the modified manuscript:

"The detailed calibration procedure is as follows: a. injected ~ 10–100 ppbv of NO<sub>2</sub> standard gas for 30 min to passivate the surfaces of the monitor and then injected dry pure air for ~ 10 min to minimize the zero point drift, which were 0.043 and 0.047 ppbv at integration times of 35 and 100 s, respectively, and resulted in LODs of CAPS of 0.13 and 0.14 ppbv (3  $\sigma$ ), respectively; b. injected a wide range of NO<sub>2</sub> mixing ratios (from 0–160 ppbv) prepared by mixing the NO<sub>2</sub> standard gas with ultrapure air into the CAPS NO<sub>2</sub> monitor and repeated the experiments three times at each NO<sub>2</sub> mixing ratio. The final results are shown in Fig. 4. To check the baseline drift of the CAPS at different humidities, we added another two sets of tests (as shown in Fig. S11) using ambient air and wet pure air and found that (a) when injecting ambient air into the CAPS (RH ranged from ~30-35%), the baseline drifts were 0.035 and 0.032 ppbv (1  $\sigma$ ) at integration times of 35 and 100 s, respectively. These baseline drifts were smaller than those when injecting dry pure air to estimate the LOD of the CAPS. We chose the largest baseline drift when injecting dry pure air to estimate the *P*(O<sub>3</sub>)<sub>met</sub> error in the following analysis; by doing this, we were able to include all the short-duration baseline drifting in the CAPS NO<sub>2</sub> monitor under different humidities."





(3) HONO production:

We added the experiments to test the HONO production in the reaction and

reference chambers under environmental conditions similar to those during the SZMGT field observations (humidity of 60-90% at the temperature ~ 20°C and  $JNO_2 \sim 0.8 \times 10^{-3} \text{ s}^{-1}$ ) at 5 L min<sup>-1</sup> sampling flow rate. We found that the HONO mixing ratios in the reaction and reference chambers were almost the same and not statistically different with that in the ambient air within the standard deviation, as shown in Fig. S9, therefore, we assume the HONO production in the reaction and reference chambers. Unfortunately, we didn't test HONO during the field observation, but we have added the modeled HONO produced from the precursors before the ambient air was injected into the NPOPR system, as described in Sect. 3.2 (page 22, lines 503-506):

"We used the output mixing ratios of the unmeasured species (i.e., OH, HO<sub>2</sub>, RO<sub>2</sub>, SO<sub>2</sub>, HONO, etc.) from the simulation in the last 1 s of the  $2^{nd}$ -stage simulation and all measured values (i.e., O<sub>3</sub>, NO, NO<sub>2</sub>, VOCs, *J* values, RH, *T*, *P*, etc.) as the model input, which were not constrained after providing initial values."

The additional HONO test results were added in the pages 11-12, lines 129-140 in the modified supplementary materials (Fig. S9), the related descriptions are added in pages 14-15, lines 328-337 in the modified manuscript:

"The HONO production in the reaction and reference chambers We tested the HONO production in the reaction and reference chambers under weather conditions similar to those during the SZMGT observations (humidity of 60-90% at a temperature of ~ 20 °C and  $J(NO_2)$  of ~ 0-8 × 10<sup>-3</sup> s<sup>-1</sup>) at a 5 L min<sup>-1</sup> sampling flow rate. We found that the HONO mixing ratios in the reaction and reference chambers were almost the same and not statistically different from that in the ambient air within the standard deviation, as shown in Fig. S9; therefore, we assumed that the HONO production in the reaction and reference chambers would not cause a significant difference in  $P(O_3)_{net}$  in the two chambers. Unfortunately, we did not test HONO during the field observation period, but we have added the modeled HONO produced from the precursors before the ambient air was injected into the NPOPR system, as described in Sect. 3.2."



Figure. S9 (a)The mixing ratios of HONO in the reaction and reference chambers and (b) the difference of HONO mixing ratios in the reaction and reference chambers.

(4) Given that some of these additional tests have not been conducted, it is difficult to assess whether the NPOPR system described here has significant improvements over other systems described in the literature.

Sorry for missing some of the calibration tests, except all the additional experiments described above, we also described the improvements of the NPOPR system described here over other systems described in the literature in page 30, lines 675-683 in the modified manuscript:

"The main improvements of NPOPR detection system compared to previous studies were as follows: (1) improved the design of the reaction and reference chambers to make sure they have good airtightness; (2) changed the air sampling structure to enable the total air flow rates change freely from 1.3 to 5 L min<sup>-1</sup> in the reaction and reference chambers, which can make the NPOPR system achieve different limits of detection (LODs) and appliable to different ambient environment; (3) characterized the NPOPR detection system at different air flow rates to optimize the  $P(O_3)_{net}$  measurements, the LODs of the NPOPR detection system are 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; (4) tested the performance of both reaction and reference chambers by combining the field measurement and

the MCM modelling method."

(5) Further, a more detailed description of the system, materials used, switching for sample analysis, etc. would be helpful for characterizing potential differences between this chamber system and others described in previous literature.

The specifications and material of the reaction and reference chambers are described in detail in S1.1. We use 1/2 PFA tubes as the NO-reaction chamber and sampling lines. We used the self-made circuit control software (Four-Channel-

Valves boxed) to control the solenoid valve to realize automatically switch the sampling lines every 2 min. We added the detailed description in page 7 lines 157-159 in the modified manuscript:

"We used homemade circuit control software (Four-Channel-Valves boxed) and a solenoid valve (001-0028-900, Parker, GER) to automatically switch the sampling lines every 2 min."

And page 7 lines 168-175:

"Igor Pro version 6 was used to calculate  $P(O_3)_{net}$  as follows: ① separate the data of the reaction and the reference chambers into two sets using the recorded valve number of 1 (reaction chamber) and 0 (reference chamber) during the sampling time; ② for each 2 min period of data, delete the first 20 s and the last 20 s when the signal was not stable, then average the rest data, and do the interpolate calculation of the reference chamber dataset; ③ calculate the difference between the Ox mixing ratios in the reaction and reference chambers (i.e.,  $\Delta O_X$ ) at the time when the reaction chamber measured Ox; ④ divide  $\Delta O_X$  by the average residence time of air in the reaction chamber  $\langle \tau \rangle$  and obtain  $P(O_3)_{net}$  at a time resolution of 4 min. "

A full error quantification and discussion of  $P(O_3)_{net}$  is missing from the manuscript's main text. Results are presented for several sensitivity tests in the main text, while results from others presented in the supplemental information. However, not all test results that influence the overall  $P(O_3)_{net}$  are included in the error budget for  $P(O_3)_{net}$ . This includes the loss of Ox in each chamber, the photo-enhanced Ox loss, residence time uncertainty, etc. A limit of detection is presented in Section 2.4, but is this then later revised in Section 3.2? Each error term in the  $P(O_3)_{net}$  are revised in Section 3.2.

We actually described the error quantification of  $P(O_3)_{net}$  when determine the LOD of the NPOPR detection system in Sect. 2.4. To make it clearer, we have changed the title of section 2.4, and reorganized the descriptions, as shown in page 16, line 372 in the modified manuscript:

<sup>"</sup>2.4 The measurement error of *P*(O<sub>3</sub>)<sub>net</sub> and the LOD of the NPOPR detection system"

And page 16 line 373:

"To assess the measurement error of  $P(O_3)_{net}$  and the LOD of the NPOPR detection system..."

And page 16 lines 377-378:

"...as three times the measurement error of  $P(O_3)_{net}$ , which was determined at a..."

And page 17 lines 393-396:

"...the  $P(O_3)_{net error}$  and LOD can be calculated using Eq. (7) and Eq. (8), respectively:



#### And page 17 lines 402-404:

"In conclusion, the LOD of the NPOPR detection system is determined to be three times  $P(O_3)_{net\_error}$ , where  $P(O_3)_{net\_error}$  is mainly determined by the measurement error of Ox (including the Ox measurement error of the CAPS NO<sub>2</sub> monitor, the light-enhanced loss of O<sub>3</sub>, and the chamber Ox losses)."

From the description above, we have included all the test results that influence the overall  $P(O_3)_{net\_error}$ , and defined them accordingly, which included the Ox measurement error of the CAPS NO<sub>2</sub> monitor, the loss of Ox in each chamber, and the photo-enhanced Ox loss, residence time uncertainty, etc. We haven't change the LOD later in Sect. 3.2, instead, we have corrected the measured data according to the errors caused by these interferences to compare them with the modeled data.

The potential for Ox loss at high RH and photo-enhanced Ox loss was discussed in supplemental information and a correction factor was devised to exclude this bias, but it is unclear how this correction factor is (or can be) used for ambient measurements; b) which RH range (30-32% is shown, but ambient RH routinely exceeds this value) was tested; c) for which flow rate regime was this correction devised and d) whether this relationship holds for all measurement scenarios. More details are needed here to fully understand the test being conducted and how it can be applied to correct  $P(O_3)_{net}$ .

Sorry for the unclear description. We have added the light-enhanced  $O_3$  loss quantification method in the modified supplementary materials in page 19, lines 226-228:

"When quantifying the light-enhanced O<sub>3</sub> loss (*d*[O<sub>3</sub>]) during ambient air measurement, we first calculate

 $\gamma$  using the measured J(O<sup>1</sup>D) and the  $\gamma$  -J(O<sup>1</sup>D) equations listed in Fig. S16a in the reaction and reference

chambers, then using the measured [O<sub>3</sub>] and Eq. S6 to calculate *d*[O<sub>3</sub>]."

The answers for the following questions are listed as follows:

b) which RH range (30-32% is shown, but ambient RH routinely exceeds this value) was tested;

We tested a wide range of RH, and we have added the O<sub>3</sub> loss experiments with humidities of 35, 50 and 75 % in Fig. S16a. We found that the  $\gamma$  -*J*(O<sup>1</sup>D) equation obtained here is also suitable for higher RH conditions. Together with the light-enhanced loss of O<sub>3</sub> as a function of RH shown in Fig. S16b, we believe that RH will not further affect the light-enhanced loss of O<sub>3</sub>.

c) for which flow rate regime was this correction devised and d) whether this relationship holds for all measurement scenarios. More details are needed here to fully understand the test being conducted and how it can be applied to correct  $P(O_3)_{net}$ .

c) and d) The flow rate was set at 5 L min<sup>-1</sup> when performing this test, which is the same as the flow rates used in the field observations. However, we also tested this relationship at other flow rates (i.e., at a flow rate of 2 L min<sup>-1</sup>) and found that this relationship was different at different flow rates, which means that we have to perform such calibration every time we use a different flow rate. We have added this statement on page 18, lines 207-208 in the supplementary materials:

"The light-enhanced loss of  $O_3$  in the reaction and reference chambers at 5 L min<sup>-1</sup> (the ambient

observation used flow rate in this study) were investigated by carrying out the following experiments: ..."

It is unclear what new information is being presented with the discussion of flow state in L282-L290 and I might suggest that this section could be removed. While the flow may be considered laminar, it is shown from residence time testing that the fluid within the chambers does not represent a "plug" flow, so reactions on the chamber walls may still produce biases in  $P(O_3)_{net}$ .

Thank you for the suggestion. We think the discussion on L282-L290 give us reasonable support for checking the flow states at different flow rates in the reaction and reference chambers; thus, we prefer to keep it like this. The fluid showed a peak at the outlet of the chamber when performing the residence time testing because we only injected high concentrations of NO<sub>2</sub> for 20 s, and its concentration showed an increase at first and then a decreasing trend due to the dilution effect. If it is a "plug" flow, the theoretical time is equal to the volume divided by the air flow rate, and the average residence time we measured was close to the theoretical time, as shown in Table S1.

Units of ppbv imply a "mixing ratio" in atmospheric chemistry terms, whereas a "concentration" is often referred to in molec cm<sup>-3</sup> or mol L<sup>-1</sup>.

Indeed, we replaced "ppbv" with "mixing ratio" throughout the manuscript.

Have the authors investigated the potential for a small amount of NO<sub>2</sub> impurity in the NO mixture used for conversion and can you address this potential bias in  $P(O_3)_{net}$ ?

During the experiments, to avoid the influence of the small amount of NO<sub>2</sub> impurity in the NO mixture used for conversion, we added a cylinder filled with partialized crystals of  $FeSO_4 \cdot 7H_2O$  to reduce NO<sub>2</sub> in the NO/N<sub>2</sub> gas cylinder to NO. We modified the related description in the modified manuscript in page 12, lines 275-277:

"To avoid the influence of small amounts of  $NO_2$  impurity in the NO standard gas used for conversion, we added a cylinder filled with partialized crystals of  $FeSO_4 \cdot 7H_2O$  to reduce  $NO_2$  in the  $NO/N_2$  gas cylinder to NO..."

To test the capacity of the particulate crystals of  $FeSO_4 \cdot 7H_2O$  to reduce  $NO_2$ , we injected ~1800 ppbv NO into the NO-reaction chamber, and tested the  $NO_2$  mixing ratios from the outlet of it using CAPS-NO<sub>2</sub> monitor, the results are shown in Fig. S13. We found that the standard deviation of  $NO_2$  mixing ratios was lower than 0.05 ppbv, which is smaller than the precision of CAPS, so we believe the particulate crystals of  $FeSO_4 \cdot 7H_2O$  performs well and the potential bias introduced by NO for  $P(O_3)_{net}$  is negligible. We modified the related description in the modified manuscript in page 12, lines 277-283:

"We injected ~1800 ppbv NO into the NO-reaction chamber and tested the NO<sub>2</sub> mixing ratios from its outlet using a CAPS NO<sub>2</sub> monitor, as shown in Fig. S13. We found that the standard deviation of the NO<sub>2</sub> mixing ratios was lower than 0.027 ppbv, which is smaller than the baseline drifts of the CAPS (which were 0.043 and 0.030 ppbv (1  $\sigma$ ) at integration times of 35 and 100 s, respectively, as mentioned in Sect. 2.3), so we believe the particulate crystals of FeSO<sub>4</sub>·7H<sub>2</sub>O performed well and the potential bias introduced by the impurity in NO mixing ratio for *P*(O<sub>3</sub>)<sub>net</sub> was negligible."



Figure. S13 Time series of NO<sub>2</sub> when injecting NO into CAPS-NO<sub>2</sub> monitor.

L330-339 addresses the fact that  $Ox (= NO_2+O_3)$  mixing ratios change over the 2 minutes sampling time of each chamber. How do the authors address issues of NO<sub>2</sub> atmospheric variability over the sampling time of the reaction versus the reference chamber, and the subtraction of these alternating two measurements, especially in urban areas? It is difficult to understand the resolution of  $P(O_3)_{net}$  in Figure 6 and how the data are averaged (or not?). Can you provide more details on how the data are processed to help the discussion?

Ox mixing ratios do slightly change over the 2 min sampling time of each chamber. To address the issues of  $NO_2$  atmospheric variability over the sampling time of the reaction versus the reference chamber, we used the interpolated Ox data in the reference chamber to make the Ox background of the reaction chamber closer to the real condition. More details are added in the modified manuscript in page7, lines 168-175:

"Igor Pro version 6 was used to calculate  $P(O_3)_{net}$  as follows: ① separate the data of the reaction and the reference chambers into two sets using the recorded valve number of 1 (reaction chamber) and 0 (reference chamber) during the sampling time; ② for each 2 min period of data, delete the first 20 s and the last 20 s when the signal was not stable, then average the rest data, and do the interpolate calculation of the reference chamber dataset; ③ calculate the difference between the Ox mixing ratios in the reaction and reference chambers (i.e.,  $\Delta O_X$ ) at the time when the reaction chamber measured Ox; ④ divide  $\Delta O_X$  by the average residence time of air in the reaction chamber  $\langle \tau \rangle$  and obtain  $P(O_3)_{net}$  at a time resolution of 4 min."

The data sets used in Fig. 6 have with a time resolution of 1 h, averaged from the

# obtained 4 min time resolution $P(O_3)_{net}$ as described above, so as to facilitate comparison with other data.

The modeling section could use some work to clarify and condense the information presented. In theory, modeling of the chemistry in both chambers separately seems like a good check on what is actually measured by the NPOPR system, but it is known from previous studies (and this issue is presented here as well) that modeling of HO<sub>2</sub> and RO<sub>2</sub> in ambient air does not match that which is measured (e.g. from Ren et al. 2013). Thus, if HO<sub>2</sub> and RO<sub>2</sub> are not well-captured in the model from parameterized VOCs and reactions therein, it is difficult to use the model to verify the chamber chemistry. Therefore, one suggestion could be to simplify this discussion to compare the ambient photochemistry from the model to the NPOPR system, given modeling limitations.

Indeed, if HO<sub>2</sub> and RO<sub>2</sub> are not well captured in the model from parameterized VOCs and reactions therein, it is difficult to use the model to verify the chamber chemistry. To evaluate  $P(O_3)_{net}$  in the ambient air, we added another model, which maintains the setup conditions of the 2<sup>nd</sup>-stage during the 3<sup>rd</sup>-stage 4-min simulation. We added the obtained  $P(O_3)_{net}$  value in the ambient air at 12:04 on 7 December to Figs. 10 and S22, which was 24.63 ppbv h<sup>-1</sup>, 1.4 ppbv h<sup>-1</sup> lower than the measured value. Therefore, we believe that the results of this simulation are more accurate and that the analysis of the simulations in the chambers can help us to assess the ozone photochemical production mechanism in the chamber.

And we added the description in page 22, lines 506-509 in the modified manuscript:

"In addition, while maintaining the setup conditions for the  $2^{nd}$ -stage of the simulation, we extended the simulation of the environment to 12:04 to obtain the modeled  $P(O_3)_{net}$  in the environment in the  $3^{rd}$ -stage simulation. The result is shown in orange marker in Fig. 10d."

and page 28, lines 627-629 in the modified manuscript:

"...which was 1.4 ppbv h<sup>-1</sup> higher than the modeled  $P(O_3)_{net}$  value in the ambient air (orange marker in

Fig. 10d, 24.6 ppbv h<sup>-1</sup>)..."

**Technical Corrections:** 

- L87: You may also choose to reference Baier et al. (2017) here for similar work.

We tested wall losses of NO<sub>2</sub> and O<sub>3</sub> in the chamber at a 5 L min<sup>-1</sup> flow rate at different humidities of 35-75 %, as well as HONO mixing ratios in the reaction and reference chambers under weather conditions similar to those during the Shenzhen observations (humidity of 60-90% while the temperature was approximately 20 °C and  $J(NO_2)$  of 0-8 × 10<sup>-3</sup> s<sup>-1</sup>), and we added the description

on page 10, lines 229-232 in the modified manuscript:

"We also tested the wall losses of NO<sub>2</sub> and O<sub>3</sub> in the chamber at a 5 L min<sup>-1</sup> flow rate at different humidities of 35-75 %, the detailed results are shown in Fig. S7 and S8, which shows that the variation in humidity effected the wall loss of NO<sub>2</sub> and O<sub>3</sub> by 0.03-0.12 % and 1.06-1.19 %, respectively, which is much smaller than the instrument detection error (which is 2 % at ambient NO<sub>2</sub> mixing ratios of 0-100 ppb) ..."

And we added the results in pages 10-11, lines 119-128 in the modified supplementary materials.

And the additional HONO test results were added in the pages 11-12, lines 129-140 in the modified supplementary materials (Fig. S9), the related descriptions are added in pages 14-15, lines 328-337 in the modified manuscript:

"The HONO production in the reaction and reference chambers We tested the HONO production in the reaction and reference chambers under weather conditions similar to those during the SZMGT observations (humidity of 60-90% at a temperature of ~ 20 °C and  $J(NO_2)$  of ~ 0-8 × 10<sup>-3</sup> s<sup>-1</sup>) at a 5 L min<sup>-1</sup> sampling flow rate. We found that the HONO mixing ratios in the reaction and reference chambers were almost the same and not statistically different from that in the ambient air within the standard deviation, as shown in Fig. S9; therefore, we assumed that the HONO production in the reaction and reference chambers would not cause a significant difference in  $P(O_3)_{net}$  in the two chambers. Unfortunately, we did not test HONO during the field observation period, but we have added the modeled HONO produced from the precursors before the ambient air was injected into the NPOPR system, as described in Sect. 3.2."

- L90: There is no Baier et al. (2021) in references. Do you mean Baier et al. (2015)?

We apologize for this mistake. We meant Baier (2015), we revised it in lines 90-92 in the modified manuscript:

"Recently, researchers have developed sensors that can directly measure  $P(O_3)_{net}$  in the atmosphere using the dual-channel chamber technique (Sadanaga et al., 2017; Cazorla et al., 2010; Baier et al., 2015 and 2017; Sklaveniti et al., 2018)..."

## And line 99:

"...the sensors developed by Cazorla et al. (2010) and Baier et al. (2015) both have an  $NO_2$ -to- $O_3$  converter unit..."

- L98: Could also benefit from citing Baier et al., 2017 for chamber artifact discussion

Yes, we have cited Baier et al. (2017) for a discussion chamber artifact in Sec. 1.3 and Sec. 1.4 in the supplementary materials. We tested the  $NO_2$  wall loss under different humidities and mixing ratios of HONO in the reaction and reference chambers as mentioned in Baier et al., (2017), and added the related discussion in the modified manuscript and supplementary materials as mentioned above.

- L107-108: please re-write for clarity

## We have revised it in lines 108-109 in the modified manuscript:

"Furthermore, all the current sensors have different degrees of wall loss of NO<sub>2</sub> and O<sub>3</sub> that can even reach 15 %, which largely affect the accuracy of the evaluation of  $P(O_3)_{net}$ ."

- L116: change "access" to assess

We changed it in line 117 in the modified manuscript:

"...which allowed us to assess the ability of the current modeling method to model  $P(O_3)_{net}$ , as described in Sect. 3."

- L131: change "amounted" to mounted

We changed it in line 132:

"...a Teflon filter was mounted before the chamber inlet to remove fine particles"

- L132: Please describe alternating flow more clearly. How do your account for the "transition" period after switching and sampling by the CAPS monitor (i.e. is some portion of the data discarded after transitioning between reaction and reference chambers as in Sklaveniti et al., 2018?)

We used CAPS NO<sub>2</sub> monitor to alternately detect the gas from the reaction and the reference chambers through the Teflon valve shown in Fig. 1. There was a transition period of about 20 s after each valve cutting, and we discarded the data

of 20 s after transitioning between reaction and reference chambers as in Sklaveniti et al., (2018), more details can be found in page 7, lines 168-175 as mentioned above.

- L141: How do you assess portability?

It consists of CAPS-NO<sub>2</sub> monitor, indoor cabinets to put the CAPS-NO<sub>2</sub> monitor, the automatic sampling system, and the automatic data sampling system, outdoor dual chambers with the push-pull base. We have assembled each part together to make it easy to transport (as shown in Fig. 1b). We added the related description in page 6, lines139-145 in the modified manuscript as follows:

"Compared to previous studies that used a dual-channel UV-absorption O<sub>3</sub> monitor (Cazorla et al., 2010) or the LIF-NO<sub>2</sub> monitor (Sadanaga et al., 2017) for Ox measurements, our choice could make the NPOPR detection system have a more stable zero-baseline and be more portable by assembling each part together, i.e., put the CAPS NO<sub>2</sub> monitor, the automatic sampling system, and the automatic data sampling system onto the indoor cabinets with the push-pull base, and put the dual chambers onto the outdoor shelf with the push-pull base."

- L186: Accuracy implies that  $P(O_3)$  is produced as it is in the atmosphere, which cannot be determined here. Better phrasing could be: "to make the NPOPR less prone to biases than other systems" or similar.

We have revised it in page 9, lines 197-198: "These efforts made the NPOPR system less

prone to biases than other systems and increased its applicability."

- L217: Please calculate the bias in  $P(O_3)_{net}$  incurred from Ox loss in the reaction and reference chamber.

We actually calculate the bias in  $P(O_3)_{net}$  incurred from Ox loss in the reaction and reference chamber when determine the LOD of the NPOPR detection system in Sect. 2.4. To make it clearer, we have changed the title of section 2.4, and reorganized the descriptions, as shown in page 16, line 372 in the modified manuscript:

"2.4 The measurement error of *P*(O<sub>3</sub>)<sub>net</sub> and the LOD of the NPOPR detection system"

And page 16 lines 373:

"To assess the measurement error of  $P(O_3)_{net}$  and the LOD of the NPOPR detection system..."

And page 16 lines 377-378:

"...as three times the measurement error of  $P(O_3)_{net}$ , which was determined at a..."

And page 17 lines 393-396:

"...the error and LOD of  $P(O_3)_{net}$  with a residence time of  $\tau$  can be calculated using Eq. (7) and Eq. (8), respectively:



And page 17 lines 402-404:

"In conclusion, the LOD of the NPOPR detection system is determined to be three times  $P(O_3)_{net\_error}$ , where  $P(O_3)_{net\_error}$  is mainly determined by the measurement error of Ox (including the Ox measurement error of the CAPS NO<sub>2</sub> monitor, the light-enhanced loss of O<sub>3</sub>, and the chamber Ox losses)."

From the description above, we have included all the test results that influence the overall  $P(O_3)_{net\_error}$ , and defined them accordingly, which included the Ox measurement error of the CAPS NO<sub>2</sub> monitor, the loss of Ox in each chamber, the photo-enhanced Ox loss, residence time uncertainty, etc.

- Table 1: is some shading missing here?

Indeed, we added shadows to  $0.019\pm0.011$  in Table 1.

- Figure 4: Typically, the axes are reversed for a calibration such that y represents known values and x represents those values that are calibrated.

Thank you for your advice. Here we make x represents known values and y represents those values that are measured by CAPS-NO<sub>2</sub> monitor, because we wanted to use this equation to access the measurement error of CAPS-NO<sub>2</sub> monitor, thus benefit us to estimate the measurement error of  $P(O_3)_{net}$ , which does not affect the analysis results of the experimental data.

- L360: Please describe what 'cd' means for readers

We have described it in line 418 in the manuscript: "...where cd indicates the light intensity

SI unit candela."

- Figure 5: Please indicate shading in a color bar, etc.

The color bar indicates the light intensity change, the lighter the color, the less light intensity. We removed the color bar in the modified manuscript as we think the color bar here is unnecessary.

- Figure 6b): is this an average of the diurnal  $P(O_3)$ 

Yes. Figure 6b) shows the average diurnal variation of different parameters (including *T*, RH,  $J_{NO2}$ ,  $J_{O1D}$ , NO, NO<sub>2</sub>, NO<sub>X</sub>, O<sub>X</sub>, O<sub>3</sub>,  $P(O_3)_{net}$ ) during 7 to 9 December 2021. We have changed the description of Fig. 6 as follows in page19, lines 441-444 in the modified manuscript:

"Figure 6: (a) Time series and (b) average diurnal variations of  $P(O_3)_{net}$ ,  $J(NO_2)$ ,  $J(O^1D)$ , T, RH, Ox, NO<sub>2</sub> and NO measured at SZMGT from 7 to 9 December 2021. The shaded areas represent the error of each measured species, where the error of  $P(O_3)_{net}$  was calculated according to the method described in Appendix II (the estimation of the  $P(O_3)_{net}$  error)."

- L432: November or December?

December. We have revised it in line 493 in the modified manuscript.

- SI L129: perhaps change the word "ingestion" to "loss?

We agree with the reviewer's suggestion. We have changed "ingestion" to "loss" in lines 366, 390, 397 in the modified manuscript, and lines 193, 207, 213, 215, 216, 229 in the modified supplementary materials.

- SI L135-136 should be Fig. S7a, not S6a

Thank you. We have checked the figure sequence again after the modifications.

- Figure S7: please add units on figure axes

Ok. We added the units in the modified supplementary materials in Fig. S16.

- Table S7a: Sklaveniti et al., 2018 does not constitute an urban area – please see description within this particular reference and check other sites as well.

Sorry for the confusion description. We have checked the observation location of Sklaveniti (2018) was at a site 2.5 km northeast of the Indiana University Bloomington campus, we have revised it in Table S10a.

- SI Tables S7a/S7b require corrections made to locations. For example, Writtle College is not located in the USA; Houston, USA should be replaced with City, State, Country format like other sites: Houston, Texas, USA, etc.

We have checked the sites and marked the revisions in yellow in Tables S10a/S10b.

## Appendix:

We have detected more errors and modified them in the manuscript, which are listed as follows:

1. We have added a co-author, Yaqing Zhou, for her help in the experiment of the HONO production.

2. We changed "minutes" to "min" in modified manuscript and the supplementary materials.

3. We changed "hours" to "h" in modified manuscript in line 374.

4. We revised the subscript of the Eq. (7) in in modified manuscript in line 395.

## References

- Baier, B. C., Brune, W. H., Lefer, B. L., Miller, D. O., and Martins, D. K.: Direct ozone production rate measurements and their use in assessing ozone source and receptor regions for Houston in 2013, Atmos. Environ., 114, 83-91, http://dx.doi.org/10.1016/j.atmosenv.2015.05.033, 2015.
- Baier B C, Brune W H, Miller D O, et al., Higher measured than modeled ozone production at increased NOx levels in the Colorado Front Range, Atmos. Chem. Phys., 17: 11273–11292, https://doi.org/10.5194/acp-17-11273-2017, 2017.
- Cazorla, M., Brune, and W. H.: Measurement of ozone production sensor, Atmos. Meas. Tech., 3, 545-555, https://doi.org/10.5194/amt-3-545-2010, 2010.
- Ren, X., van Duin, D., Cazorla, M., Chen, S., Mao, J., Zhang, L., Brune, W. H., Flynn, J. H., Grossberg, N., Lefer, B. L., Rappenglück, B., Wong, K. W., Tsai, C., Stutz, J., Dibb, J. E., Thomas Jobson, B., Luke, W. T., and Kelley, P.: Atmospheric oxidation chemistry and ozone production: results from SHARP 2009 in Houston, Texas, J. Geophys. Res.-Atmos., 118, 5770-5780, https://doi.org/10.1002/jgrd.50342, 2013.
- Sadanaga, Y., Kawasaki, S., Tanaka, Y., Kajii, Y., and Bandow, H.: New system for measuring the photochemical ozone production rate in the atmosphere, Environ. Sci. Technol., 51, 2871-2878, https://doi.org/10.1021/acs.est.6b04639, 2017.
- Sklaveniti, S., Locoge, N., Stevens, P. S., Wood, E., Kundu, S., and Dusanter, S.: Development of an instrument for direct ozone production rate measurements: measurement reliability and current limitations, Atmos. Meas. Tech., 11, 741-761, https://doi.org/10.5194/amt-11-741-2018, 2018.