Response to reviewers' comments

RC1:

This manuscript reports on the development of an instrument for measuring ozone production rates in the atmosphere. While this type of instrument was already published in the literature, the authors present an interesting approach to account for wall effects that were found to significantly impact the measurement accuracy . Such developments are scarce for this technique and this work is of interest for the scientific community.

However, the writing must be revised. It was not easy to read this publication, the meaning of a large number of sentences being difficult to understand. A few examples are provided below but there are other instances in the text. In addition, the authors should address the specific comments indicated below.

This reviewer recommends major revisions with a second round of reviews.

Response: Many thanks for revision suggestions. We have conducted a major revision to clarify key technique details and improve writing clarity. A point-to-point response is also prepared.

Examples of confusing words/terminology

- L35: changed to "imperfect"
- L38 & L188: changed to "control experiments"
- L65: changed to "photochemical production"
- L102 changed to "box model constrained with observations"
- L165: changed to "parallel measurements"
- L221: "constrained with comprehensive measurement of parameters concerning O_3 photochemistry"

Examples of sentences that are difficult to read, unclear, which need to be rephrased

- L43-44: "… fairly active O_3 photochemistry, which was assisted by a high abundance of VOCs and NO_x, atypically high Mea-OPR even under high-NO_x conditions, but mediated by relatively weak ultraviolet (UV) radiation."
- L125-126: "Measurement uncertainties in O_x might be enlarged as transferred to be the measurement uncertainties in ΔO_x, thus further amplifying the measurement uncertainties of Mea-OPR in a unit of ppbv h^{-1} because the gas residence time in Mea-OPR chambers is typically much shorter than 1 hour."
- Entire section 2.2

Response: Revisions are shown as follows:

- L35: changed to "imperfect"
- L38 & L286: changed to "control experiments"
- L66: changed to "photochemical production"
- L107: changed to "box model constrained with observations"
- L253: changed to "parallel measurements"
- L368: "constrained with comprehensive measurements of parameters concerning O_3 photochemistry"
- L43-44: The sentence is deleted.
- L125-126: Please refer to revision in lines 137-139.
- Entire section 2.2: Please refer to revision in lines 286-388.

Specific comments:

- L 146-148: The authors discuss how O_x losses change between raw quartz material and Teflon coated material. The authors should provide quantitative information here, referencing Table S3 from the supplementary material.

Response: Suggestions are followed. Please refer to our revision in lines 164-165 "Corresponding uptake coefficient of O_3, γ_{O3}, is calculated in this context to be 5.2×10^{-9} on Teflon wall surface and 7.1×10^{-8} on quartz surface."

- L149 Eq. 4: Please define the parameters in the text.

Response: Please refer to our revision in lines 167-169 "where ΔO_3, uptake is the differential O_3 between the ambient and the chamber due to uptake loss of O_3 in the chamber. $O_{3, amb}$ is the ambient O_3 concentration in ppbv. ω_{O3} represents the mean molecular velocity of O_3, in m s^{-1}. τ is the mean gas residence time in the chamber in second."

- L150: "To date, these effective designs have not yet been integrated and evaluated in a state-of-the-art version of Mea-OPR" – The authors should clarify what is meant here by "effective designs".

Response: We added in lines 171-172 "All in all, previous studies recommend wall materials of high light transmittance for the reaction chamber, precise and stable instrument to measure ΔO_x, and suppression of wall effect by employing inert material and large diameter of the chamber."

- Section 2.1: The authors should provide more details on this new OPR system. How is ambient air introduced into the chambers? What type of inlet? What type of Teflon coating (brand)? What type of UV filter for the reference chamber? How is the sampling performed from the chambers? What type of outlets? It seems from Figure S1 that some air is also extracted from the chambers using MFCs and a pump. How is it done? Sampling flow rates from O_3 and NO_2 monitors?

- L171-172: "The instrument alignment experiment suggested that nigttime ΔO_x was 0.07 (± 0.26) ppbv, within the instrument detection limits (Fig. S5)." – How did the authors get the number of 0.07 ppb? Is it an average value for the whole time series? If so, it should be clarified. Looking at Fig. S5, it is clear that ΔO_3 and ΔNO_2 display a similar increasing trend over the whole time period (total increase of approximately 0.4 ppb). Is it due to a drift in the monitors' zero? If so, why is it similar for both types of monitors?

Response: The increasing trend is possibly a result of small differences between two adjacent calibrations of O_3 analyzer and NO_x analyzer or drifts of instrument zero. Nighttime ΔO_x is an average value for the whole time series. Please refer to our revision in lines 259-260 "The campaign average of ΔO_x is 0.07 (± 0.26) ppbv in fact within the instrument detection limits of 1.0 ppbv for O_3 analyzer."

- L178-180: "Another key design to suppress the wall effect was the transparent Teflon coating, which was essential for accurate Mea-OPR by reducing the uptake coefficient of O3 from 10^{-8} on quartz wall (Sklaveniti et al., 2018) to 10^{-9} on Teflon coating wall under dark conditions." – The authors should also address how the uptake of NO_2 changes between quartz and Teflon. It is likely that the NO_2 uptake is larger for Teflon since this material is more hydrophilic than quartz.

Response: Great idea! The revison is shown in lines 199-202 "In addition, slight suppression on uptake coefficient of NO_2 (γ_{NO2}) of 6.3×10^{-8} on Teflon coating wall in the reference chamber for our system under dark conditions relative to report value of 7.0×10^{-8} on quartz wall is also evidential (Sklaveniti et al., 2018; Sadanaga et al., 2017)."

- L187 Eq. 5: This equation must be demonstrated and the authors should add a section in the supplementary material to present how they derived it. Is "φ_{trans}" for the reaction chamber only? If so, please clarify it in the text. What are the assumptions made to derive this equation? It seems that the authors consider that Mea-OPR scales linearly with "$\varphi(trans)$" and "$\varphi(\Delta HONO$ or $\Delta NO_x)$". The authors should discuss the validity of these assumptions. This equation also deserves more discussion in the main paper to highlight how wall losses of O_3, UV transmission and surface production of HONO are corrected for. Why did the authors decided to not include a correction for NO_2 wall losses?

Response: Indeed! We added a paragraph to explain our measurement definition and correction of Mea-OPR. Revisions in lines 266-285 are shown.

- Section 2.2 : This section needs major revisions. This reviewer had difficulties to understand what was done here. In addition, indicating that the production of HONO is due to the heterogeneous hydrolysis of NO_2 is too restrictive. Light-induced processes leading to the conversion of NO_2 into HONO at the chamber's surface should be discussed.

Response: Please refer to our revision in line 336 "Uptake loss of NO_2 and HONO production from NO_2 uptake (R1) or unknown sources on the Teflon film and quartz surface" and lines 513-515 "Daytime source of HONO in zero-OPR control experiment has suggested that this source depended on chamber contamination rather than NO_2 concentration. Both heterogeneous uptake of NO_2 and unknown source of HONO might account for the daytime HONO production."

L220: The authors mention that "MCM model was conducted to calculate O_3 production in chambers". However, there is no information about the model used in this work. The authors should add a section in the supplementary material to provide details about the model, the chemical mechanism, and how the model was constrained.

Response: We added a paragraph to describe the model construction and constraint. Please refer to our revision in lines 377-388.

- L228-231: "Under typical working conditions of Mea-OPR, O_3 uptake loss contributes to a false Mea-OPR signal of 20.3 ppbv h^{-1} at uptake coefficient of 7.11×10^{-8} and S/V ratio of 18 m^{-1} (the least in the literature), relative to a false Mea-OPR signal of 1.29 ppbv h^{-1} at uptake coefficient of 8.12×10^{-9} and S/V ratio of 9.76 m^{-1} in our Mea-OPR, assuming ambient O_3 concentration of 50 ppbv." – This comparison does not seem pertinent. When Sklaveniti et al. report a potential bias of approximately 20 ppb/h at an ozone mixing ratio of 50 ppb, this is for daytime conditions when the photo-enhanced loss of ozone is operating in the reaction chamber. For the present instrument, the uptake coefficient taken into consideration is for dark conditions. As the authors indicate on L234-235, the O_3 uptake coefficient for daytime conditions is approximately one order of magnitude larger, which would lead to a "false Mea-OPR signal" of 12.9 ppb/h. So, while an improvement is indeed observed, the magnitude of this improvement is not as large as stated.

Response: We have added a Table 1 to compare our results with previous reports. Also, measurement bias associated with O_3 uptake for our Mea-OPR in nighttime and daytime are comprehensive discussed in lines 464-468 "It is the difference in γ_{O3} between the two chambers that brings bias for ΔO_x measurements. The difference in γ_{O3} of 4.6×10^{-9} ($\pm 2.0 \times 10^{-9}$) is ca. one third of γ_{O3} in the reaction chamber under dark conditions. ΔO_x measurement bias of 0.78 (± 0.85) ppbv h^{-1} is then calculated for our Mea-OPR during our field campaign. Correction of this measurement bias brings Mea-OPR of -0.46 (± 0.75) ppbv h^{-1} to 0.31 (± 0.92) ppbv h^{-1} in the nighttime during the field campaign." and lines 482-494.

- L239-241: "A routine water flush cleaning and UV-photochemical-aging cleaning of both chambers were then scheduled after occurrence of heavy pollution episodes" – Nothing is said about the effectiveness of these cleaning periods. The authors should discuss whether these were useful to reduce the ozone uptake on the chambers' wall.

Response: So far, we have conducted 5 zero-OPR control experiments and have measured uptake coefficient from 8.0×10^{-8} to 4.0×10^{-7} under the $j(O^1D)$ of 1.0×10^{-5} s^{-1}. The high uptake coefficient is collected after heavy pollution episodes while the lowest uptake coefficient is collected after our cleaning procedures. Our cleaning procedures are very effective in

suppression of O_3 uptake loss. The zero-OPR control experiments on date 14-16 November, 2023 (before cleaning) and 30 November-2 December, 2023 (after cleaning) are shown in Fig. R1 as an example.
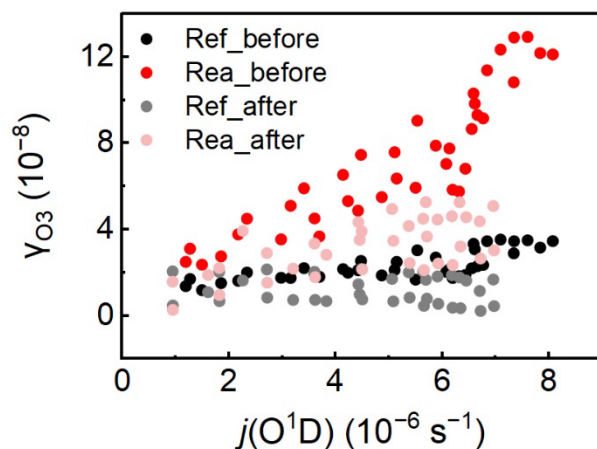

Figure R1: The relationship between γ_{O_3} and $j(O^1D)$ during two zero-OPR control experiments on 14-16 November, 2023 (before) and 30 November-2 December, 2023 (after), respectively. "Before" represent the zero-OPR control experiment conducted before cleaning. "After" is the zero-OPR control experiment conducted after cleaning. It can be seen that the uptake coefficient of O_3 is reduced by half after cleaning.

- L258-260: "After multiple control experiments (not shown), we could also assume the uptake coefficient of O_3 being stable between two adjacent control experiments." – These results are important to ensure that the correction parameterized through Eqs. 7-10 is suitable for the whole campaign. The authors should show and discuss these additional experiments in the supplementary material.

Response: We conducted two adjacent zero-OPR control experiments on 5-6 January, 2023 and 14-15 March, 2023. It can be seen from Fig. R2 that the uptake coefficient of O_3 barely changes during two-month field campaign. Thus, we could assume the uptake coefficient of O_3 being stable in our field campaign from 5 February to 3 March, 2022. In general, we recommend at least one zero-OPR control experiment for a four-week field campaign and chamber cleaning after heavy pollution episodes or before a new field campaign.
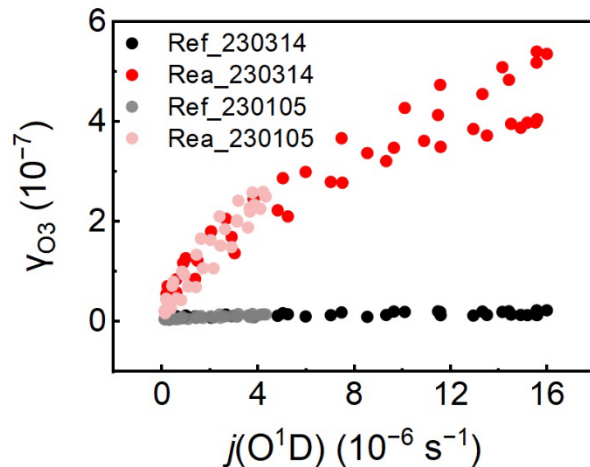
Figure R2: The relationship between γ_{O_3} and $j(O^1D)$ in two adjacent zero-OPR control experiments (5-6 January, 2023 and 14-15 March, 2023). It can be seen that the uptake coefficient of O_3 barely changes during two-month field campaign.

- L261-263: Eqs. 7-8 do not account for the potential impact of RH on the O_3 uptake. The reviewer understands that deriving the RH-dependence during daytime is challenging due to fast changes in $j(O^1D)$. However, since several "control experiments" were performed, wouldn't it be possible to group all the results to investigate the RH-dependence within bins of J-values?

Response: Great idea. We calculate the fitting residual by subtracting the data points to the fitting line. The fitting residual shows no dependence on RH in daytime (Figure R3). Therefore, multiple regression fitting for uptake coefficient concerning its dependence on $j(O^1D)$ and RH isn't done.
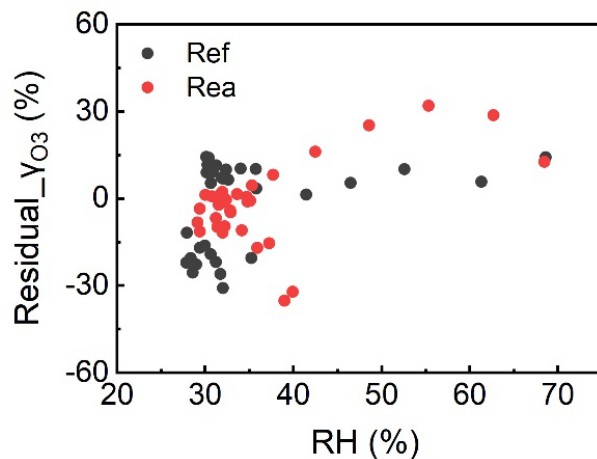

Figure R3: Plot of fitting relative residual in Fig 3c and RH during zero-OPR control experiments (5–6 February, 2022). Uptake coefficient- $j(O^1D)$ fitting shows a high uncertainty in low $j(O^1D)$ conditions. However, fitting residual is randomly distributed, rather than depends on RH.

- L269-271: "Despite of considerable uptake coefficient of NO_2, compared with that of O_3, much lower NO_2 level (12.9 ppbv) relative to O_3 inferred negligible wall loss of NO_2, which was transferred to ca. 1.79 ppbv h−1 false signal of Mea-OPR at most during the 1-week HONO production experiment." – Do the authors mean that the loss of NO_2 at the surface leads to a negligible loss of O_x species? If so, this should be clarified. In addition, the stated bias is similar, even larger, than that reported for the dark O_3 wall loss on L230. So, how could it be negligible? Do the authors mean that this is negligible compared to the light-induced O_3 wall loss?

Response: This has been clarified in lines 496-502 "In the 1-week HONO production experiment, net NO_x uptake loss reached 1.00 (±0.65) and 0.76 (±0.65) ppbv in the reaction and reference chamber, relative to the ambient (Fig. 5a). Uptake coefficient of NO_2 in the reaction chamber and reference chamber are calculated 8.3×10^{-8} and 6.3×10^{-8}, which is actually comparable to daytime uptake of O_3 and slightly less than previous measurement of NO_2 uptake on quartz chamber of 7.0×10^{-8} (Sklaveniti et al., 2018). Due to the lack of light-dependence, differential NO_2 uptake between the two chambers is much less, compared with differential O_3 uptake. Much lower NO_2 level (14.7 ppbv vs 28.7 ppbv) than O_3 during our field campaign also rationalizes much lower measurement bias associated with NO_2 uptake. Eventually, measurement bias of 0.72 ppbv h^{-1} for Mea-OPR is calculated."

- L279-280: "RH in the reaction chamber scattered at approximately 61% (±14%) and was much higher than the ambient air of 36% (±14%) during the nighttime" – How do the authors explain that RH in the reaction chamber could be significantly larger than in ambient air?

Response: This has been corrected and clarified in Figure S3.

- L281-282: The authors should consider to show how the HONO uptake varies during the night as they did for O3 in Fig. 1b. This could be included in the supplementary material. Did the authors investigate whether the HONO uptake depends on environmental variables such as T and RH?

Response: We agree with the reviewer that uptake and releasing of HONO is interesting. As seen Fig. R4, HONO uptake depends on its concentration, reflecting a partitioning equilibrium among HONO and particulate nitrite deposited on chamber wall. This result will be further summarized in a separate manuscript.
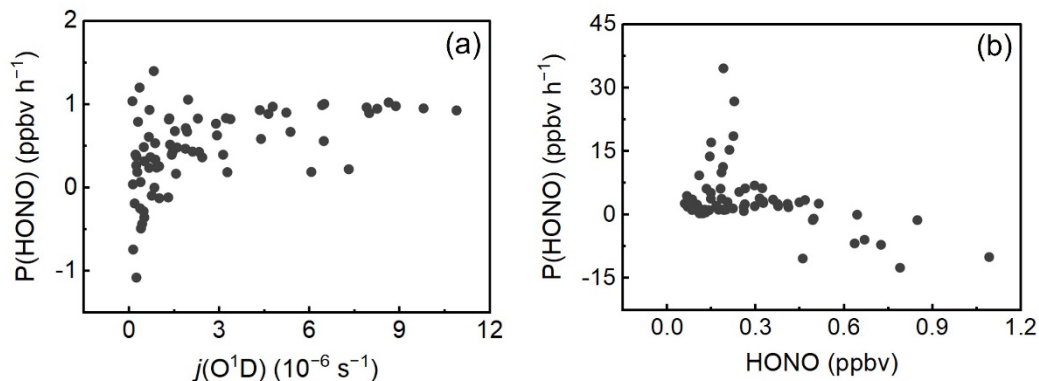
Figure R4: Plot of HONO production, P(HONO), in the reaction chamber againest (a) $j(O^1D)$ and (b) HONO measurements in the ambient.

- L304-305: "Currently, NO_2 uptake and HONO production correction are not applied for our Mea-OPR." – If corrections are not applied, the term "$\varphi(\Delta HONO$ or $\Delta NOx)$" should be removed from Eq. 5.

Response: We take the advices of reviewers to include all the corrections in Eq. 5. We have added a new paragraph to state our measurement definition of Mea-OPR in lines 266-285.

- L322-323: "Evaluated from 1-hour consistency measurements every night, the measurement uncertainties for ΔNO_2 and ΔO_3 are $\pm 3.8\%$ and $\pm 1.1\%$" – Do these errors only account for drifts in monitors' zero? Or do they factor other sources of uncertainties such as errors associated to the calibrations reported in Table S2 and the concentration of the calibration gases?

Response: Yes, both shift in responding sensitivity and instrument zero might contribute to the measurement uncertainties for ΔNO_2 and ΔO_3. Higher uncertainties at low levels of NO_x and O_3 also suggests that baseline shift might be mainly responsible for this measurement uncertainty.

We have revised in line 559-561 "Higher uncertainties are found at low levels of NO_x or O_3, which suggests that continuous improvement in ΔO_x measurement precision will benefit our measurement."

- Section 3.4: The authors should consider showing and discussing the entire OPR time series in addition to the mean diel profile. Discussing the day-to-day variability of OPR and NO_x would nicely complement Fig. 4.

Response: We agree with reviewer on more detailed discussion on Mea-OPR and its response with precursor concentrations, meterological parameters, etc. In another prepared manuscript, we compare our measurements in two cities (Beijing and Lhasa), and shows distinct O_3 photochemistry in these two urban environments. OVOCs or OVOCs/NO_x ratio in the two cities appears to account for distinct O_3 photochemistry. With the restriction of manuscript lengthen and writing scope, we only choose to show the potential of our Mea-OPR system to characterize O_3 photochemistry in urban environments.

- Figure 3: The authors should add an additional panel to show ozone production rates that would be calculated when the O_3 wall loss is not corrected for. What is the magnitude of the correction?

Response: The corrections associated with O_3 wall loss is essential for Mea-OPR. This also identifies the major uncertainties of Mea-OPR as shown (Fig. 4 in the context). Similarly, the corrections associated with NO_2 wall loss is also a considerable part of Mea-OPR.

- Figure 4: The reviewer recommends using another color coding for NO. The datapoints close to 80 ppb NO are not visible.

Response: Suggestions are accepted.

- The recent publication from Morino et al. (Atmos. Environ., 309, 2023) is not referenced and the authors may want to include it.

Response: Suggestions are accepted.

Edits:

- L118: "… or named MOPS in literature" should read ""… or named MOPS or OPR instrument in the literature"

- L135-136: "Sklaveniti et al. (2018) estimated that O_3 uptake loss in their version of Mea-OPR would lead to false Mea-OPR signal of ~20 ppbv h^{-1} assuming ambient O_3 to be 50 ppbv." Should read "Sklaveniti et al. (2018) estimated that a photo-enhanced O_3 uptake in their version of Mea-OPR would lead to false Mea-OPR signal of ~20 ppbv h−1 assuming ambient O_3 to be 50 ppbv."

- L141: "is usually chosen for it is easier to manipulate" should read "is usually chosen since it is easier to manipulate"

- L177-178: "… while enabling multiple sampling instruments equipped" should read "while enabling the sampling from several instruments"

- L321: "contribute to uncertainties of −4% and −5%, respectively" should read "contribute to a systematic bias of −4% and −5%, respectively

Response: Suggestions are accepted.