Response to reviewers’ comments

RC2:

The manuscript "Optimizing a twin-chamber system for direct ozone production rate measurement" by Wang et al. presents an instrument designed to measure directly the total in-situ ozone production. This is indeed a measurement that could be useful to improve our understanding of ozone formation. Instruments such as this have been described in the past, and deployed in the field with varying degrees of success. The authors claim to have substantially improved the technique over previous designs and to be able to achieve a detection limit of 2.8 ppb/h with a 27% uncertainty. This would be a great development, but I don't see in this manuscript much evidence to back the authors' claims, to be honest.

For the most part, the paper is written rather confusingly. The description of the characterization experiments is severely lacking details, and the information provided is limited to 1 day or diurnal averages. This is not sufficient to allow proper evaluation of the instrument's performance or the author's claims. Additionally, the characterization experiments are not described properly. The text and the figures suggest that the instrument was sampling ambient air for these experiments which would not be a good method to characterize a new instrument. One would want to do this type of experiments under controlled conditions, with air of known composition, especially if the goal is to demonstrate improved performance. At the moment, I cannot recommend publication because I see several serious methodological errors that undermine the authors' claims.

Response: Many thanks for the suggestions. We have revised the manuscript accordingly and included key content originally in supplementary material to clarify these points mentioned by reviewers. A point-to-point response is also presented.

Specific comments

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In section 3.1, it is said that during the zero NOx high O3 experiments the wall loss was more than 3x higher in the reaction chamber than in the reference chamber. This seems a pretty significant factor to me that could have large impact on the instrument's performance. I think the authors should elaborate on the possible causes (is it the teflon film? differences in humidity?), and also comment on the effect on the measurements. Was this difference constant through the measurement period? Impossible to say from the data presented here.

Response: The dependence of O3 wall loss on $j(O^1D)$ suggests that photo-enhanced uptake of O3 on chamber wall or deposited aerosol on chamber wall might account for differential uptake between the two chambers. The fitting between uptake coefficient-$j(O^1D)$ is found to be well, with a fitting residual larger than 12.7% of $\gamma_{03}$ in the morning and dawn, but less than 2.0% of
$\gamma_{O3}$ during the noontime. The fitting residual shows no dependence on RH in zero-OPR control experiments (Fig. R1). Please refer to our revision in lines 454-458.

Figure R1: 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.

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.

Figure R2: The relationship between $\gamma_{O3}$ 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.
A "routine water flush" to eliminate particles from the chamber is mentioned on page 8. First of all, if this is only done after "severe pollution episodes" it is not routine and, second, what were the criteria to decide when was it needed? More importantly, I would expect this procedure to have an important impact on the wall interactions of Ox. Presumably, it will lead to higher presence of water on the surfaces and therefore more issues with the wall loss and/or HONO production.

Response: Please refer to our revision in lines 440-444 “A water flush cleaning and UV-photochemical-aging cleaning of both chambers are then scheduled before new field campaign or after occurrence of heavy pollution episodes (PM$_{2.5}$ $>$ 80 µg cm$^{-3}$), following the recommendation in previous literature (Chu et al., 2022). Water flush cleaning is found effective to remove deposited aerosol particles on chamber wall. UV-photochemical-aging cleaning not only dry the chamber, also deactivated the wall surface. The two-step cleaning process is found to effectively reduce wall loss of Ox to a lower rate of this report (not shown).”

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. R3 as an example.

Figure R3: The relationship between $\gamma_{O_3}$ 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” represents 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.

Overall, it is not possible to assess the authors' claim that their procedures lead to improved performance of the instrument based on just one day of observations shown here, especially since they look like ambient observations.

Response: We clarified the design and data analysis zero-OPR control experiment in the revised manuscript. Please refer to lines 288-334 “As Mea-OPR system samples the ambient air, wall loss and photochemical production of O$_3$ are occurring simultaneously. Therefore, these two processes cannot be decoupled from each other. A control experiment sampling diluted O$_3$ standard gas (generated from zero air passing through ozone generator) has been designed and
conducted. O$_3$ is diluted to around 113 ppbv by zero air before entering the chambers. High O$_3$ concentration in zero-OPR experiments facilitates measurements of O$_3$ wall loss. Due to extremely low NO$_x$ and low VOCs in the zero-air supply, suppressed O$_3$ photochemistry, apart from O$_3$ photolysis, in the reaction chamber is assumed. The control experiment is thus referred as zero-OPR control experiment. Zero-OPR experiments have been conducted for several field campaigns so far. Other zero-OPR control experiments measure changes of O$_3$ uptake in winter when heavy haze, i.e. PM$_{2.5}$ > 80 μg m$^{-3}$ (Chu et al., 2022), occurs frequently in Beijing (not shown). This might lead to the contamination of the chamber (Sklaveniti et al., 2018). Therefore, we recommend each zero-OPR control experiment at least during one field campaign to check the O$_3$ wall loss. Herein, results from zero-OPR control experiment conducted on 5-6 March, 2022 during the first employment of our Mea-OPR in Beijing are shown as an example in the context. Before the O$_3$ enters both chambers, another O$_3$ analyzer monitors the diluted O$_3$ standard gas, referred as O$_3$, amb. An excess flow rate of 1.0 L min$^{-1}$ is to maintain 1 bar pressure in the quartz chamber. O$_3$ travels through chambers and is then sampled via the main outlets to measure O$_3$ concentration in the two chambers. Measurements of O$_3$, NO$_2$, NO (Thermo Scientific, Model 42i, LOD: 0.4 ppbv), HONO and CO (Thermo Scientific, Model 48i, LOD: 0.04 ppmv) in chambers have been simultaneously conducted in control experiments (Fig. 2). The measurements of other species are to check the experiment control of O$_3$ precursors in zero-OPR control experiments……"
It appears (line 225) that the model was used to calculate the photochemical production of O\textsubscript{3} and to estimate the O\textsubscript{3} wall loss by subtracting it from the instrument's output. First of all, it is not clear at all that this is what has been done, and the authors should describe the procedure more accurately. But, if this is the case, I see a major issue with this procedure because it relies on the assumption that an MCM model can predict O\textsubscript{3} production with great accuracy. This is most likely not true, especially under ambient conditions (which the following paragraph, lines 234-246, suggest was the case), and in particular it will not be true with the level of accuracy that would be required to estimate the uptake coefficients in the chambers to the degree that the authors claim. Using a model in this way undermines the whole discussion on O\textsubscript{3} uptake in Section 3.1.

Response: We have clarified this issue in lines 414-428 “As shown in Fig. 3, evident O\textsubscript{3} uptake loss was observed in both chambers and higher O\textsubscript{3} uptake loss was observed in the reaction chamber (\(\Delta\text{O}_3 = 7.7\) ppbv) relative to the reference chamber (\(\Delta\text{O}_3 = 2.3\) ppbv) at noon. \text{NO}_x concentration was measured around 0.03–1.05 ppbv in the zero-OPR control experiment. A slight increase in \text{NO}_x from the morning to the noon is accompanying increasing \(j(O^1D)\). Also, a stable and low concentration of \text{NO}_x in the zero air before entering the chamber further confirms our attribution of this bridge-shaped \text{NO}_x to previously-identified unknown source of HONO and \text{NO}_x in Teflon chamber (Rohrer et al., 2005; Akimoto et al., 1987; Ye et al., 2016). MCM model is then conducted to calculate O\textsubscript{3} production, OPR\textsubscript{zero}, in both chambers for the zero-OPR control experiment. MCM model is believed to be able to well represent O\textsubscript{3} photochemistry in the relatively simple chemical reaction system involving mainly oxidation of CO. OPR\textsubscript{zero} in the reference chamber is calculated near zero at noon because stray light in the reference chamber was too weak to be meaningful for O\textsubscript{3} photochemistry. In addition, abundance of O\textsubscript{3} chemical precursors in reference chamber during the zero-OPR control experiments are relatively low. Therefore, O\textsubscript{3} loss in the reference chamber is not corrected. OPR\textsubscript{zero} in the reaction chamber is calculated to be up to 9.0 (±1.5) ppbv h\textsuperscript{−1} at noon (Fig. S6). \(\Delta\text{O}_3\), uptake in the reaction chamber is therefore corrected for non-zero OPR\textsubscript{zero} in the reaction chamber and the correction comprised 28% of \(\Delta\text{O}_3\), uptake. As OPR\textsubscript{zero} is much less than \(\Delta\text{O}_3\), uptake, O\textsubscript{3} photochemical production is still considered to be successfully controlled in the zero-OPR control experiment.”

For MCM model, we have clarified this issue in lines 329-332 “Simulations of ambient OPR are somewhat suffering from uncertainties tied to for example imperfect understanding on oxidation mechanism of complex NHMC (Saunders et al., 2003; Hao et al., 2023). Notably, OPR\textsubscript{zero} simulations by our chemical model are more trustful, relative to simulations of ambient OPR, as simple O\textsubscript{3} photochemistry involving only oxidation of CO, but not complex NHMC, is of concerns in the zero-OPR control experiment.”

In section 3.2, the authors discuss the formation of HONO in the instrument chambers. Again it is not clear what was done and how during this "1 week HONO experiment". It is also not clear whether HONO was measured or calculated, and how. If the numbers on HONO production cited on page 10 come from the MCM model (which parametrization/reaction scheme?), then I have serious doubts on their reliability.
Response: Please refer to our revision in lines 336-388 for a more detailed description of 1-week HONO experiment and data processing procedure. “Uptake loss of NO2 and HONO production from NO2 uptake (R1) or unknown sources on the Teflon film and quartz surface have been proposed to be error source of Mea-OPR by Baier et al. (2015) and Sklaveniti et al. (2018). Similar to O3 uptake, uptake of NO2 is a potential measurement bias of ∆O3. Moreover, wall loss of NOx and production of HONO specially in the reaction chambers perturb O3 photochemistry therein. To obtain uptake loss of NOx and production of HONO in both chambers, additional measurements of HONO and NOx in the ambient and in the chambers has been conducted for one week during 10–18 February, 2022. HONO was measured by customized LOPAP. The detailed description of customized LOPAP can be found in Wang et al. (2023). Three sets of identical HONO instruments sample ambient air and chamber air simultaneously. Measurements of chamber HONO allow us to calculate differential HONO between chambers and differential HONO between chambers and the ambient (not shown). This control experiment to characterize NO2 uptake and HONO production in the reaction is conducted during the field application of Mea-OPR. To discriminate it from the month-long field campaign, we refer this control experiment as 1-week HONO production experiment in the context……”

In any case, I disagree very much with their conclusion that this is not an important factor. The authors estimate an uptake coefficient for NO2 of the order of 10^-8 (line 268), which is of the same magnitude as their estimate of O3 uptake coefficient (figure 1). Therefore I think the claim that the wall loss of NO2 (which likely leads to HONO formation) is negligible does not hold. It is also quite apparent from figure 2 that while the NOx levels in both chambers are similar, HONO levels are not which strongly suggest there is formation in one chamber.

Response: We agree with the reviewer and include these corrections in Mea-OPR (Eq. 5) in the revised manuscript. We have further clarified this point in lines 266-282 “Mea-OPR can be calculated in Eq. (5), which is modified from previous scheme in the literature (Cazorla and Brune, 2010; Sadanaga et al., 2017; Sklaveniti et al., 2018). ∆NO2 and ∆O3 are the differential NO2 and O3 between the two chambers, respectively. D is the diameter of chambers in m. O3, amb and NO2, amb represent the ambient O3 and NO2 concentration in ppbv, respectively. φtrans is the ratio of in-chamber j(O1D) to ambient j(O1D) as determined by the UV transmittance of the two Mea-OPR chambers. We assume linear dependence of OPR on j(O1D) (Tan et al., 2018a), and therefore Mea-OPR underestimation on ambient OPR associated with chamber filter of UV in the reaction chamber and stray light in the reference chamber can be corrected by φtrans. Positive ∆HONO in the daytime is found in our field campaign due to NO2 uptake or unknown chamber source of HONO (Rohrer et al., 2005; Akimoto et al., 1987; Ye et al., 2016). As a result, Mea-OPR tends to be overestimated with a correction factor of φHONO typically higher than unit. Negative ∆NOx is observed in our field campaign due to uptake loss of NO2 on chamber wall. This leads to bias in ∆Ox measurements and also reaction chamber underestimation of ambient O3 production. As a result, Mea-OPR tend to underestimate OPR with a correction factor of φNOx typically lower than unit. In addition, chamber formation of HONO is somewhat associated with uptake loss of NO2, therefore φHONO and φNOx are evaluated together. The overall correction factor associated with imperfect chamber mimic of ambient O3 photochemistry
due to $\Delta\text{HONO}$ and $\Delta\text{NO}_x$ is defined as $\phi_{\text{HONO}, \Delta\text{HONO}} and $\phi_{\text{NO}_x, \Delta\text{NO}_x}$. 

represents correction of $\Delta\text{O}_3$ due to the uptake loss of $\text{O}_3$ on the two chambers. Analogy correction, $\phi_{\text{NO}_2, \Delta\text{NO}_2} = \frac{\gamma_{\text{NO}_2, \text{Rea}} \cdot \omega_{\text{NO}_2, \text{Rea}} - \gamma_{\text{NO}_2, \text{Ref}} \cdot \omega_{\text{NO}_2, \text{Ref}}}{\gamma_{\text{NO}_2, \text{Ref}} \cdot \omega_{\text{NO}_2, \text{Ref}}} \cdot \text{NO}_2, \text{amb}$, due to uptake loss of $\text{NO}_2$ also applies. In our field campaign, correction due to uptake loss of $\text{NO}_2$ is much less, relative to the correction associated with $\text{O}_3$ uptake loss.”

If HONO is generated inside the chamber it will not only release NO (which may not affect the total $\text{O}_3$ balance if it just interconvert $\text{O}_3$ to $\text{NO}_2$) but also OH which most definitely will lead to increased $\text{O}_3$ production inside one of the chambers. I don’t see how the authors can be sure that HONO production on the chamber walls is not an issue in their system (lines 304).

Response: We have further clarified this point. Please refer to our revision in lines 504-537 “In the 1-week HONO production experiment, uptake loss of HONO during the nighttime were surprisingly spotted, together with production of HONO during the daytime (Fig. 5b). Nighttime loss of HONO on the wall surface ($\Delta\text{HONO} = \text{HONO}_{\text{amb}} - \text{HONO}_{\text{inchamber}}$, $\Delta\text{HONO} = 0.14 (\pm 0.28)$ and 0.004 (±0.30) ppbv for the reaction chamber and reference chamber relative to the ambient), is not suspected. Sklaveniti et al. (2018) reported HONO production rate of up to 9 ppbv h$^{-1}$ with uptake loss of $\text{NO}_2$ of 66 ppbv h$^{-1}$ under dark conditions, giving a yield of HONO of 0.14. Even assuming a yield of 0.14 from uptake of $\text{NO}_2$, production of HONO would reach 0.42 and 0.28 ppbv h$^{-1}$ in the reaction and reference chamber, ca. $\Delta\text{HONO} = -0.14$ and $-0.093$ ppbv. HONO uptake on aerosol particles at night might account for the HONO loss here (Ren et al., 2020). RH in the reaction chamber scatters at approximately 50% (±13%), which might lead to deliquescence of deposited aerosol particles on the wall surface. As the temperature rose and RH dropped in the early morning, uptake loss of HONO on the wall surface is diminishing. Further decrease in the zenith angle even led to production of HONO in both chambers, resulting in $\Delta\text{HONO} = -0.11 (\pm 0.16)$ and $-0.27 (\pm 0.12)$ ppbv for the reaction chamber and reference chamber. Daytime source of HONO in zero-OPR control experiment has suggested that this source depended on chamber contamination rather than $\text{NO}_2$ concentration. Both heterogeneous uptake of $\text{NO}_2$ and unknown source of HONO might account for the daytime HONO production. Daytime $\Delta\text{HONO}$ herein appeared to be much less than previous reports of 20 ppbv h$^{-1}$ for laboratory conditions (Quartz surface, $\text{NO}_2 = 100$ ppbv) (Sklaveniti et al., 2018) and of 11–36 ppbv h$^{-1}$ in the ambient of Houston (Quartz surface, $\text{NO}_2 = 50$ ppbv) (Baier et al., 2015). The inert Teflon surface coating and possible cleaner chamber in our Mea-OPR system might account for much less daytime $\Delta\text{HONO}$.

While $\text{NO}_2$ uptake and HONO production mechanism are not totally accounted for, we carry on our theme discussion on their potential perturbation on $\text{O}_3$ photochemistry in the chamber. As calculated in Model S1-S2, in which ambient HONO ($\text{HONO}_{\text{amb}}$) and HONO in the reaction chamber ($\text{HONO}_{\text{Rea}}$) is constrained, $\text{O}_3$ production overestimation owing to HONO production in the reaction chamber is 5.4% on average during the 1-week HONO production experiment (not shown). The influence of HONO production on Mea-OPR is much weaker than previous reports (Baier et al., 2015; Sklaveniti et al., 2018). More detailed exploring of $\text{O}_3$ photochemistry suggests that HONO photolysis comprises 17.6% of the total primary ROX source budget for the ambient, while comprises 23.0% of the total primary ROX source budget for the reaction.
chamber. The overall primary ROx source budget is averaged 8.8% higher in the reaction chamber than in the ambient air, which reflects that ΔHONO does considerably perturb the ROx source budget and therefore O3 production. In our model, not all RO2 or HO2 results in O3 production (Tan et al., 2018b; Ma et al., 2022), which accounts for lower percent of Mea-OPR perturbation than ROx budget perturbation by HONO production. In the previous study in Houston, HONO photolysis comprises 29% of the total primary HOx source budget for the ambient, while comprises 40% of the total primary HOx source budget in the reaction chamber (Czader et al., 2012). Much less contribution of HONO photolysis to overall production of peroxy radical in Beijing (Lu et al., 2013) and much less ΔHONO for our Mea-OPR therefore accounts for much weaker perturbation on OPR in the reaction chamber. As calculated in Model S3, in which HONO\textsubscript{Rea} and NOx\textsubscript{Rea} are constrained, O3 production overestimation in the reaction chamber is 9.4% (Fig. 5c).”

Minor Comments

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Equation 5: how is this derived?

Response: Please refer to line 266-282 “Mea-OPR can be calculated in Eq. (5), which is modified from previous scheme in the literature (Cazorla and Brune, 2010; Sadanaga et al., 2017; Sklaveniti et al., 2018). ΔNO2 and ΔO3 are the differential NO2 and O3 between the two chambers, respectively. D is the diameter of chambers in m. O3, amb and NO2, amb represent the ambient O3 and NO2 concentration in ppbv, respectively. \( \varphi_{\text{trans}} \) is the ratio of in-chamber \( j(O^1D) \) to ambient \( j(O^1D) \) as determined by the UV transmittance of the two Mea-OPR chambers. We assume linear dependence of OPR on \( j(O^1D) \) (Tan et al., 2018a), and therefore Mea-OPR underestimation on ambient OPR associated with chamber filter of UV in the reaction chamber and stray light in the reference chamber can be corrected by \( \varphi_{\text{trans}} \). Positive ΔHONO in the daytime is found in our field campaign due to NO2 uptake or unknown chamber source of HONO (Rohrer et al., 2005; Akimoto et al., 1987; Ye et al., 2016). As a result, Mea-OPR tends to be overestimated with a correction factor of \( \varphi_{\Delta\text{HONO}} \) typically higher than unit. Negative ΔNOx is observed in our field campaign due to uptake loss of NO2 on chamber wall. This leads to bias in ΔOx measurements and also reaction chamber underestimation of ambient O3 production. As a result, Mea-OPR tend to underestimate OPR with a correction factor of \( \varphi_{\Delta\text{NOx}} \) typically lower than unit. In addition, chamber formation of HONO is somewhat associated with uptake loss of NO2, therefore \( \varphi_{\Delta\text{HONO}} \) and \( \varphi_{\Delta\text{NOx}} \) are evaluated together. The overall correction factor associated with imperfect chamber mimic of ambient O3 photochemistry due to ΔHONO and ΔNOx is defined as

\[
\varphi_{\Delta\text{HONO}} \cdot \frac{(\gamma_{O_3, \text{Rea}} - \gamma_{O_3, \text{Ref}}) \cdot O_3, \text{amb}}{D}
\]

represents correction of ΔO3 due to the uptake loss of O3 on the two chambers. Analogy correction,

\[
\varphi_{\Delta\text{NOx}} \cdot \frac{(\gamma_{NO_2, \text{Rea}} - \gamma_{NO_2, \text{Ref}}) \cdot NO_2, \text{amb}}{D}
\]

due to uptake loss of NO2 also applies. In our field
campaign, correction due to uptake loss of NO$_2$ is much less, relative to the correction associated with O$_3$ uptake loss.”

Figure S1: I would suggest to move this figure to the main text. And also to add a proper description of the instrument in the main text.

Response: Suggestion is accepted!