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

In section 3.1, it is said that during the zero NO_x high O_3 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 O_3 wall loss on $j(O^1D)$ suggests that photo-enhanced uptake of O_3 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 γ_{O3} in the morning and dawn, but less than 2.0% of

γ_{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.
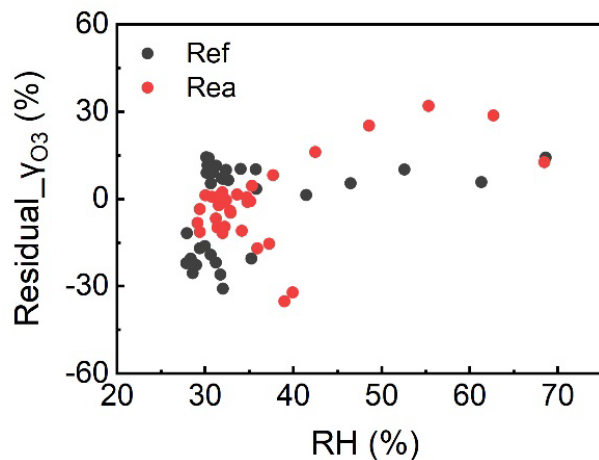

Figure R1: Plot of fitting relative residual in Fig 3c and RH during zero-OPR control experiments (5–6 February, 2022). Uptake coefficient- $j(O^1D)$ fitting shows a high uncertainty in low $j(O^1D)$ conditions. However, fitting residual is randomly distributed, rather than depends on RH.

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.
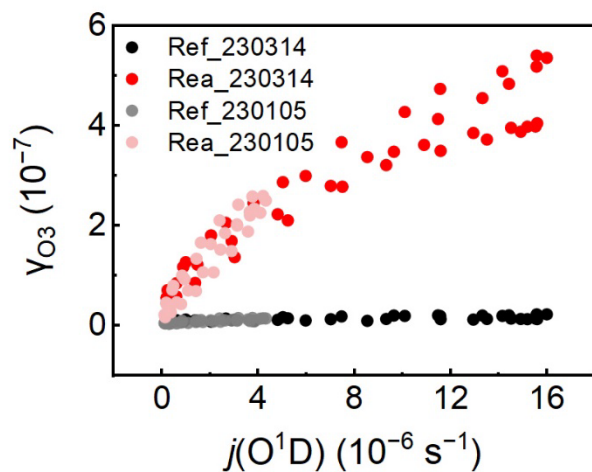

Figure R2: The relationship between γ_{O_3} and $j(O^1D)$ in two adjacent zero-OPR control experiments (5-6 January, 2023 and 14-15 March, 2023). It can be seen that the uptake coefficient of O_3 barely changes during two-month field campaign.

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 O_x. 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 O_x 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.
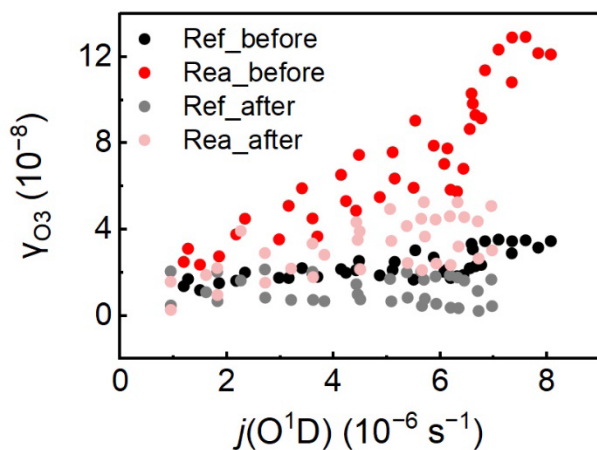

Figure R3: The relationship between γ_{O_3} and $j(O^1D)$ during two zero-OPR control experiments on 14-16 November, 2023 (before) and 30 November-2 December, 2023 (after), respectively. "Before" represents the zero-OPR control experiment conducted before cleaning. "After" is the zero-OPR control experiment 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……"

I don't understand this sentence on page 8: "The MCM model was conducted to calculate O_3 production in chambers". There has been no mention of a model in previous pages. How was the model constructed and run? It seems that the model was constrained to NO_x and CO (or just initialized, please clarify what is meant with "prescribed"), but there is no information on the other parameters: VOCs, humidity, photolysis rates etc... Some of this information is in the supporting information but it should be at least referred to.

Response: We have moved the method section originally in the supplementary material into the main context of our manuscript. We have also added a new paragraph to describe model construction and model constraint. Please refer to revision in lines 377-388 "Mechanisms are extracted from the website of Leeds University (MCM v3.3.1, http://mcm.leeds.ac.uk/MCM) for our chemical model to mimic the oxidation of VOCs and inorganic species in the chamber. Uptake of O_3 or uptake of NO_2 or HONO production are not included in the model as O_3, NO_x and HONO are constrained with our measurements. For simulation of zero-OPR control experiments in Model S0, only oxidation of CO is calculated by the model, as oxidation of VOCs are not expected in the zero-OPR control experiments. For simulation of 1-week HONO production experiments in Model S1–S3, oxidations of measured VOCs and model-generated photochemical intermediates are calculated. The preliminary model run (not shown) suggests that k_{OH} contributed by NO_x, CO, VOCs, OVOCs, and model-generated intermediates underestimates the measured k_{OH}. This indicates a missing k_{OH} as compared with k_{OH} measurements, which has been described in Wei et al.(2020). Additional formaldehyde (HCHO) and HCHO + OH reaction is then included in chemical model to represent the missing k_{OH} and better represent O_3 chemistry (Tan et al., 2021). Model constraints include measurements of HONO, NO_x, O_3, CO, VOCs, OVOCs, j values, T, RH, etc."

It appears (line 225) that the model was used to calculate the photochemical production of O_3 and to estimate the O_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_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_3 uptake in Section 3.1.

Response: We have clarified this issue in lines 414-428 "As shown in Fig. 3, evident O_3 uptake loss was observed in both chambers and higher O_3 uptake loss was observed in the reaction chamber (ΔO_3 = 7.7 ppbv) relative to the reference chamber (ΔO_3 = 2.3 ppbv) at noon. NO_x concentration was measured around 0.03–1.05 ppbv in the zero-OPR control experiment. A slight increase in NO_x from the morning to the noon is accompanying increasing $j(O^1D)$. Also, a stable and low concentration of NO_x in the zero air before entering the chamber further confirms our attribution of this bridge-shaped NO_x to previously-identified unknown source of HONO and 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_3 production, OPR_{zero}, in both chambers for the zero-OPR control experiment. MCM model is believed to be able to well represent O_3 photochemistry in the relatively simple chemical reaction system involving mainly oxidation of CO. OPR_{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_3 photochemistry. In addition, abundance of O_3 chemical precursors in reference chamber during the zero-OPR control experiments are relatively low. Therefore, O_3 loss in the reference chamber is not corrected. OPR_{zero} in the reaction chamber is calculated to be up to 9.0 ($\pm$1.5) ppbv h^{-1} at noon (Fig. S6). $\Delta O_{3,\,uptake}$ in the reaction chamber is therefore corrected for non-zero OPR_{zero} in the reaction chamber and the correction comprised 28% of $\Delta O_{3,\,uptake}$. As OPR_{zero} is much less than $\Delta O_{3,\,uptake}$, O_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_{zero} simulations by our chemical model are more trustful, relative to simulations of ambient OPR, as simple O_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 NO_2 and HONO production from NO_2 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 O_3 uptake, uptake of NO_2 is a potential measurement bias of ΔO_x. Moreover, wall loss of NO_x and production of HONO specially in the reaction chambers perturb O_3 photochemistry therein. To obtain uptake loss of NO_x and production of HONO in both chambers, additional measurements of HONO and NO_x 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 NO_2 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 NO_2 of the order of 10^{-8} (line 268), which is of the same magnitude as their estimate of O_3 uptake coefficient (figure 1). Therefore I think the claim that the wall loss of NO_2 (which likely leads to HONO formation) is negligible does not hold. It is also quite apparent from figure 2 that while the NO_x 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). ΔNO_2 and ΔO_3 are the differential NO_2 and O_3 between the two chambers, respectively. D is the diameter of chambers in m. $O_{3, amb}$ and $NO_{2, amb}$ represent the ambient O_3 and NO_2 concentration in ppbv, respectively. φ_{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 φ_{trans}. Positive ΔHONO in the daytime is found in our field campaign due to NO_2 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 $\varphi_{\Delta HONO}$ typically higher than unit. Negative ΔNO_x is observed in our field campaign due to uptake loss of NO_2 on chamber wall. This leads to bias in ΔO_x measurements and also reaction chamber underestimation of ambient O_3 production. As a result, Mea-OPR tend to underestimate OPR with a correction factor of $\varphi_{\Delta NO_x}$ typically lower than unit. In addition, chamber formation of HONO is somewhat associated with uptake loss of NO_2, therefore $\varphi_{\Delta HONO}$ and $\varphi_{\Delta NO_x}$ are evaluated together. The overall correction factor associated with imperfect chamber mimic of ambient O_3 photochemistry

due to ΔHONO and ΔNO$_x$ is defined as $\varphi_{\Delta HONO\ and\ \Delta NO_x} \cdot \dfrac{(\gamma_{O_3,\ Rea} \cdot \omega_{O_3,\ Rea} - \gamma_{O_3,\ Ref} \cdot \omega_{O_3,\ Ref}) \cdot O_{3,\ amb}}{D}$ represents correction of ΔO$_3$ due to the uptake loss of O$_3$ on the two chambers. Analogy correction, $\dfrac{(\gamma_{NO_2,\ Rea} \cdot \omega_{NO_2,\ Rea} - \gamma_{NO_2,\ Ref} \cdot \omega_{NO_2,\ Ref}) \cdot NO_{2,\ amb}}{D}$, due to uptake loss of NO$_2$ 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."

If HONO is generated inside the chamber it will not only release NO (which may not affect the total O$_x$ balance if it just interconvert O$_3$ to NO$_2$) but also OH which most definitely will lead to increased 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 (ΔHONO = HONO$_{amb}$ – HONO$_{inchamber}$, ΔHONO = 0.14 (±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 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 NO$_2$, production of HONO would reach 0.42 and 0.28 ppbv h^{-1} in the reaction and reference chamber, $ca.$ ΔHONO = −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 (ΔHONO = −0.11 (±0.16) and −0.27 (±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 NO$_2$ concentration. Both heterogeneous uptake of NO$_2$ and unknown source of HONO might account for the daytime HONO production. Daytime ΔHONO herein appeared to be much less than previous reports of 20 ppbv h^{-1} for laboratory conditions (Quartz surface, NO$_2$ = 100 ppbv) (Sklaveniti et al., 2018) and of 11–36 ppbv h^{-1} in the ambient of Houston (Quartz surface, 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 ΔHONO.

While NO$_2$ uptake and HONO production mechanism are not totally accounted for, we carry on our theme discussion on their potential perturbation on O$_3$ photochemistry in the chamber. As calculated in Model S1-S2, in which ambient HONO (HONO$_{amb}$) and HONO in the reaction chamber (HONO$_{Rea}$) is constrained, 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 O$_3$ photochemistry suggests that HONO photolysis comprises 17.6% of the total primary RO$_x$ source budget for the ambient, while comprises 23.0% of the total primary RO$_x$ source budget for the reaction

chamber. The overall primary RO_x source budget is averaged 8.8% higher in the reaction chamber than in the ambient air, which reflects that $\Delta HONO$ does considerably perturb the RO_x source budget and therefore O_3 production. In our model, not all RO_2 or HO_2 results in O_3 production (Tan et al., 2018b; Ma et al., 2022), which accounts for lower percent of Mea-OPR perturbation than RO_x budget perturbation by HONO production. In the previous study in Houston, HONO photolysis comprises 29% of the total primary HO_x source budget for the ambient, while comprises 40% of the total primary HO_x 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 $\Delta HONO$ for our Mea-OPR therefore accounts for much weaker perturbation on OPR in the reaction chamber. As calculated in Model S3, in which $HONO_{Rea}$ and $NO_{x, Rea}$ are constrained, O_3 production overestimation in the reaction chamber is 9.4% (Fig. 5c)."

Minor Comments

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). ΔNO_2 and ΔO_3 are the differential NO_2 and O_3 between the two chambers, respectively. D is the diameter of chambers in m. $O_{3, amb}$ and $NO_{2, amb}$ represent the ambient O_3 and NO_2 concentration in ppbv, respectively. φ_{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 φ_{trans}. Positive $\Delta HONO$ in the daytime is found in our field campaign due to NO_2 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 $\varphi_{\Delta HONO}$ typically higher than unit. Negative ΔNO_x is observed in our field campaign due to uptake loss of NO_2 on chamber wall. This leads to bias in ΔO_x measurements and also reaction chamber underestimation of ambient O_3 production. As a result, Mea-OPR tend to underestimate OPR with a correction factor of $\varphi_{\Delta NO_x}$ typically lower than unit. In addition, chamber formation of HONO is somewhat associated with uptake loss of NO_2, therefore $\varphi_{\Delta HONO}$ and $\varphi_{\Delta NO_x}$ are evaluated together. The overall correction factor associated with imperfect chamber mimic of ambient O_3 photochemistry due to $\Delta HONO$ and ΔNO_x is defined as $\varphi_{\Delta HONO \text{ and } \Delta NO_x} \cdot \dfrac{(\gamma_{O_3, Rea} \cdot \omega_{O_3, Rea} - \gamma_{O_3, Ref} \cdot \omega_{O_3, Ref}) \cdot O_{3, amb}}{D}$ represents correction of ΔO_3 due to the uptake loss of O_3 on the two chambers. Analogy correction, $\dfrac{(\gamma_{NO_2, Rea} \cdot \omega_{NO_2, Rea} - \gamma_{NO_2, Ref} \cdot \omega_{NO_2, Ref}) \cdot NO_{2, amb}}{D}$, due to uptake loss of NO_2 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!