Response to comments

Reviewer 1:

General comments: The authors report a self-constructed PERCA-CEAS system for RO_2 measurement and its application during a field campaign in Zhuhai for more than 15 days. $P(O_3)$ was calculated and the local photochemical production of O_3 was evaluated based on measurements. The instrument represents a valuable tool for investigating atmospheric chemistry. However, the manuscript still requires some revisions to better clarify the innovations of the instrument, methodology, and scientific findings.*

Response: We appreciate the reviewer for the careful reading and their constructive comments on our manuscript. Below, we provide a point-by-point response to each of the reviewer's concerns. **As detailed below, the reviewer's comments are in** *italicized font*, **our response to the comments are shown as** normal font**. New or modified texts are in** blue**.**

Comment [1-1]: *To better demonstrate the advantages of the instrument presented in this study, a summary table comparing different RO_2* measurement techniques is recommended, particularly the PERCA-based methods developed in previous studies. The table should include key parameters such as chemical chain length, detection limit, and instrument weight, as well as their respective advantages and disadvantages.*

Response [1-1]: Thanks for the suggestion. A summary table has been compiled to compare our PERCA-CEAS system against previously reported PERCA-based methods, covering key metrics such as calibration sources, chain length, detection limits, operating pressure and measurement uncertainties.

We have added this comprehensive comparison table and supplemented the related information in Section 3.1.

"The optimal CL for the PERCA-CEAS measurement system was determined to be 30±2 under the conditions of RH = 10%, NO = 8 ppm, and CO = 8% based on the pure HO_2 calibration. Calibration using a mixed radical source consisting of 50% HO_2 and 50% CH_3O_2 yielded a CL of 24±1 under the same conditions. As summarized in Table 1, the obtained CL is lower than values reported in most previous PERCA studies, which were typically above 50 and occasionally exceeded 200 (e.g., George et al., 2020; Wood and Charest, 2014). The differences in CL are primarily attributed to wall loss of HO_2 radicals due to reactor material, reactor design and working pressure. Although the obtained CL is relatively low compared with these PERCA instruments, the results demonstrate that the developed PERCA-CEAS system provides stable and reliable sensitivity for atmospheric RO_2* measurements.

Table 1. Summary of performance for reported PERCA measurement systems

Measurement System	Channel Configuration	Calibration Source	CL	LOD	Uncertainty	Pressure (mbar)	Reference
PERCA-luminox	Single	CH_3O_2	200-260	2 pptv	40%	400 ~ 1000	(Green et al., 2003)
PERCA-luminol	Dual	HO_2 50%HO_2+50%CH_3O_2	45±7	3±2 pptv (3σ)	/	200	(Kartal et al., 2010)
PERCA-luminol	Dual	HO_2 50%HO_2+50%CH_3O_2	88±17 64±18	3 pptv (1σ)	/	300	(Horstjann et al., 2014)
PERCA-CRDS	Dual	HO_2	150±50	10 pptv (3σ)	/	1000	(Liu et al., 2009)
PERCA-CRDS	Dual	HO_2 CH_3O_2	200 180	4 pptv (3σ)	/	1000	(Liu and Zhang, 2014)
PERCA-CRDS	Dual	HO_2 50%HO_2+50%CH_3O_2	62 ± 9	< 2 pptv	15%	200 ~ 350	(George et al., 2020)
PERCA-CRDS	Dual	HO_2 RO_2*	55	0.9 pptv (3σ)	/	1000	(Duncianu et al., 2020)
PERCA-CAPS	Dual	$CH_3C(O)O_2$ CH_3O_2	168±20	0.6 pptv (1σ, 60s)	25%	1000	(Wood and Charest, 2014)
ECHAMP-CAPS	Dual	$CH_3C(O)O_2$ CH_3O_2	17	2.5 pptv (1σ, 90s)	27%	1000	(Wood et al., 2017)
PERCA-IBBCEAS	Dual	HO_2	91±11	0.9 pptv (1σ)	16-20%	1000	(Chen et al., 2016)
PERCA-CEAS	Single	HO_2 50%HO_2+50%CH_3O_2	30±2 24±1	0.38 pptv (1σ)	18.4-25.7%	1000	This work

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Comment [1-2]: *The instrument was only applied for continuous measurement of about 15 days. How would it perform for longer-term measurements?*

Response [1-2]: To further evaluate long-term performance, the instrument was subsequently deployed in a two-month field campaign. For illustration, the attached figure R1 shows the time series of our measurements during the two-month campaign. Over the two-month deployment, the instrument showed stable performance, with no noticeable loss in CEAS mirror reflectivity or need for major optical realignment and recalibration. Routine maintenance was limited to replacing filters and silica gel every 3–4 days. These results demonstrate that the instrument is suitable for long-term continuous measurements.

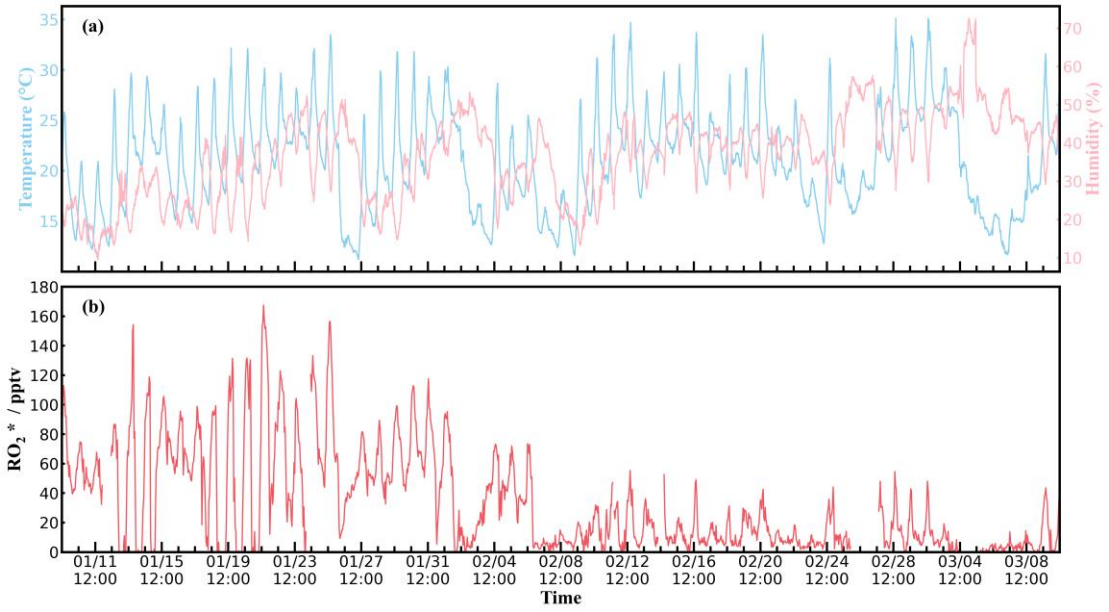

Figure R1. Time series of (a) temperature and relative humidity, and (b) RO_2* radical concentration during the two-month field campaign.

Comment [1-3]: *Local production and transport contributions to O_3 were estimated based on the measurements in this study. The results suggest that O_3 enhancement was primarily driven by local production, while regional transport mainly played an export role. However, source-oriented chemical transport model simulations have shown that O_3 is less affected by local emissions than by regional transport (Gong et al., 2021), which appears to be inconsistent with the conclusions of this study. Moreover, process analysis has also indicated that vertical mixing can contribute more to surface O_3 than chemical production (Mathur et al., 2018). Please provide possible explanations for the discrepancies between the results of this study and those reported by three-dimensional chemical transport models, and evaluate the reliability and limitations of the conclusions drawn in this work.*

Response [1-3]: Thanks for your suggestion. Gong et al., (2021) focused on the Yangtze River Delta during the spring–summer transition, whereas our observations were conducted in November in the Pearl River Delta under prevailing northeasterly monsoon conditions. During the campaign, the Zhuhai site was located downwind of the highly urbanized inner PRD region. Transport of air masses from the inner PRD was accompanied by continuous photochemical O_3 production, leading to elevated O_3 levels at the coastal site. Located at the southern edge of the PRD under prevailing northeasterly flow, Zhuhai effectively represented a regional outflow site, where O_3-rich air masses were further transported toward the South China Sea.

In addition, the transport term in our budget analysis, $R(O_3)$ is defined as a residual term in the budget closure framework, which inherently aggregates all unresolved physical processes, including horizontal advection, vertical mixing, and dry deposition. Therefore, the influence of vertical entrainment discussed in CTM studies, such as Mathur et al., (2018), is inherently included within our diagnosed transport contribution. While Mathur et al. mainly emphasized the role of vertical mixing in the early morning

buildup of O_3, our analysis focuses on the processes contributing to the formation of surface O_3. During the observation, there was no significant enhancement of O_3 concentration after the break down of nocturnal boundary layer in the early morning, distinct from the case when vertical mixing from residual layer occurs.

We also acknowledge the limitations associated with the calculation of $P(O_3)_{net}$, which are mainly related to uncertainties in RO_2* measurements, the approximation of k_{eff}, and the upper limit of $D(O_3)$. Based on uncertainty propagation, the overall uncertainty in $P(O_3)_{net}$ was estimated to be approximately 21.5-28.0%. This uncertainty analysis has been added and clarified in the revised manuscript.

"Considering uncertainties associated with RO_2* measurements (18.4-25.7%), the approximation of k_{eff} (~10%), and the upper limit of $D(O_3)$ level (5%), the overall uncertainty in $P(O_3)_{net}$ was estimated to be approximately 21.5-28.0%."

Comment [1-4]: *$P(O_3)$ was approximated as $P(O_3)_{net}$ in this study, because $D(O_3)$ was estimated to be ~0.7 ppb, and $P(O_3)$net always has positive contribution. However, chemical process has negative contribution to O_3 during nighttime due to NO titration. Therefore, the estimation of local and regional transport contribution to O_3 has large uncertainties using this method.*

Response [1-4]: Thanks for pointing out this issue. Our calculation of $P(O_3)$ based on $k_{eff}[RO_2^*][NO]$ specifically represents the photochemical production rate. Therefore, nighttime NO titration should not have been included in our calculation by using RO_2* measurements. To correct for this issue, we have excluded all nighttime data (18:00–06:00) for $P(O_3)$ calculation in the revised manuscript. Accordingly, we have updated the calculations and the corresponding results in Figure 3, Figure 5 and Figure 6.

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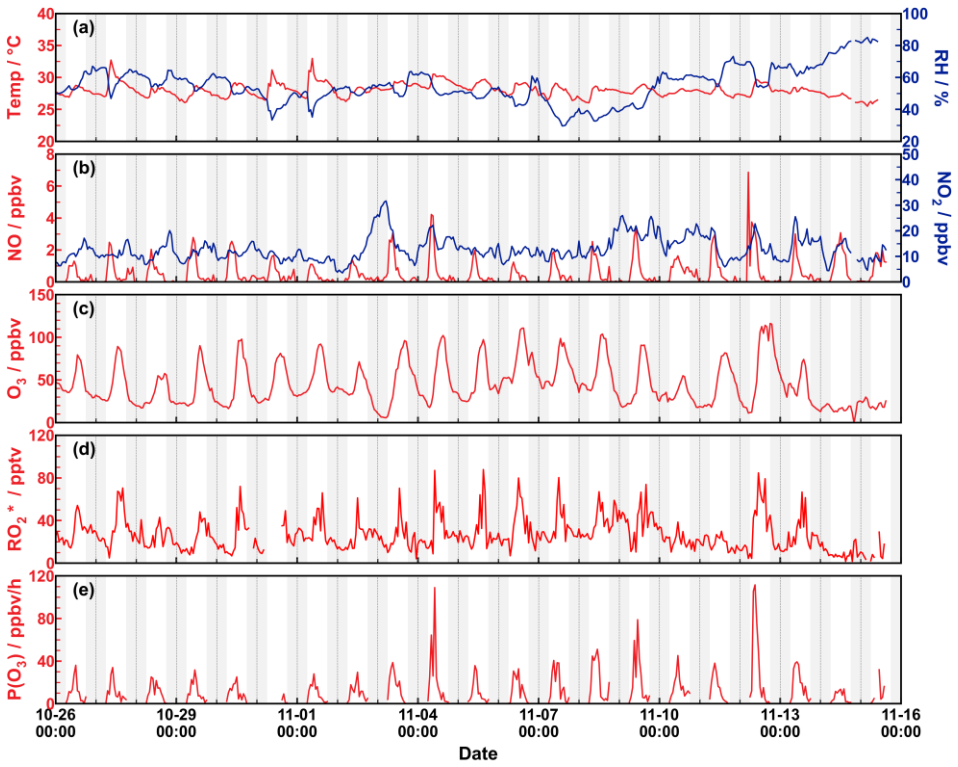

Figure 3. Time series of meteorological parameters (T, RH), major pollutants (O_3, NOx, RO_2*), and daytime $P(O_3)$ (06:00–18:00) during the autumn observation period of 2024, with a temporal resolution of 1 hour.

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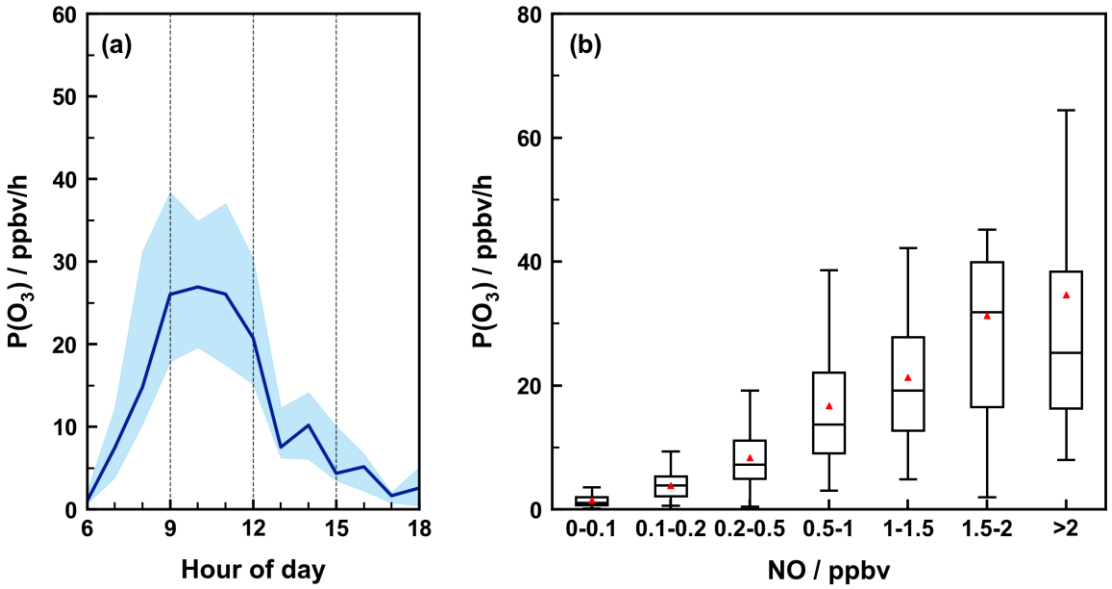

Figure 5. Diurnal variation and NO-dependent distribution of daytime $P(O_3)$. (a) Average diurnal profile of daytime $P(O_3)$ during the observation period. The dark line denotes the median, and the light blue shading indicates the interquartile range (25th–75th percentile). (b) Box plots of daytime $P(O_3)$ under different NO concentration ranges. The black line inside each box represents the median, and the red triangle marks the mean value within each interval.

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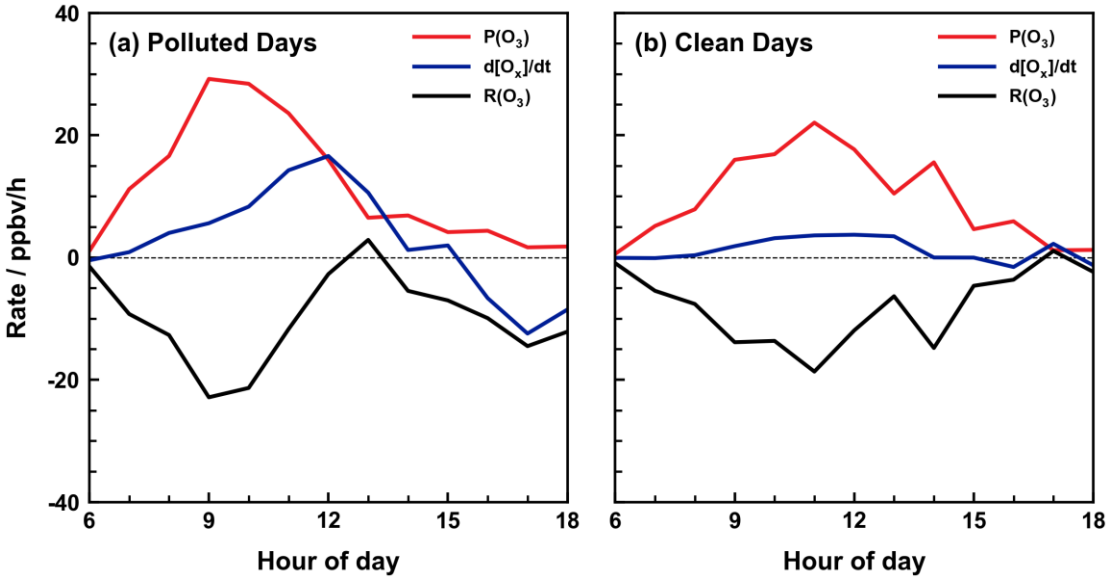

Figure 6. Diurnal variations of daytime $P(O_3)$, d[Ox]/dt, and $R(O_3)$ during (a) polluted and (b) clean periods. The red line represents the photochemical ozone production rate $P(O_3)$, the blue line indicates the rate of change of total oxidants d[Ox]/dt, and the black line corresponds to the regional

transport rate $R(O_3)$.

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Comment [1-5]: *Line 119: “analyzing” should be corrected as “analyze”.*
Response [1-5]: We have corrected “analyzing” to “analyze”.

Comment [1-6]: Line 217: “time” should be corrected as “times”.
Response [1-6]: We have corrected “time” to “times”.

Comment [1-7]: Line 299: “show” should be corrected as “showed”.
Response [1-7]: We have corrected “show” to “showed”.

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