

Response to comments

Referee #1:

General comments: The authors report a self-constructed PERCA-CEAS system for RO₂ measurement and its application during a field campaign in Zhuhai for more than 15 days. P(O₃) was calculated and the local photochemical production of O₃ 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 RO₂* 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 HO₂ calibration. Calibration using a mixed radical source consisting of 50% HO₂ and 50% CH₃O₂ 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 HO₂ 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 RO₂* 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 ₃ O ₂	200-260	2 pptv	40%	400 ~ 1000	(Green et al., 2003)
PERCA-luminol	Dual	HO ₂ 50%HO ₂ +50%CH ₃ O ₂	45±7	3±2 pptv (3σ)	/	200	(Kartal et al., 2010)
PERCA-luminol	Dual	HO ₂ 50%HO ₂ +50%CH ₃ O 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 ₃ O ₂	200 180	4 pptv (3σ)	/	1000	(Liu and Zhang, 2014)
PERCA-CRDS	Dual	HO ₂ 50%HO ₂ +50%CH ₃ O 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 ₃ C(O)O ₂ CH ₃ O ₂	168±20	0.6 pptv (1σ, 60s)	25%	1000	(Wood and Charest, 2014)
ECHAMP-CAPS	Dual	CH ₃ C(O)O ₂ CH ₃ O 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 ₃ O 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.

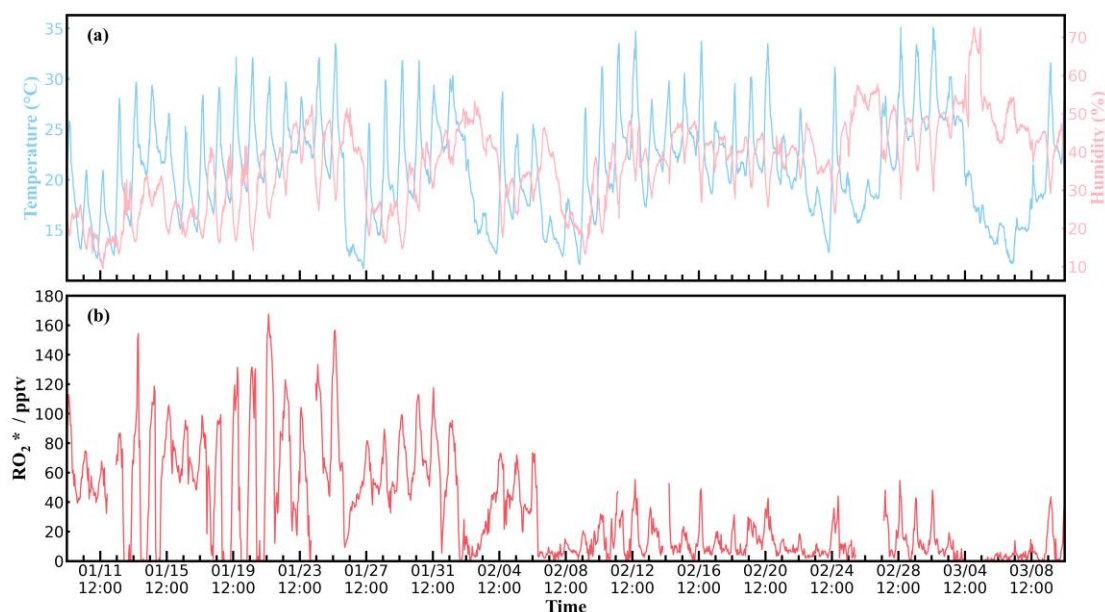


Figure R1. Time series of (a) temperature and relative humidity, and (b) RO_2^* radical concentration during the two-month field campaign.

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, $R(\text{O}_3)$ 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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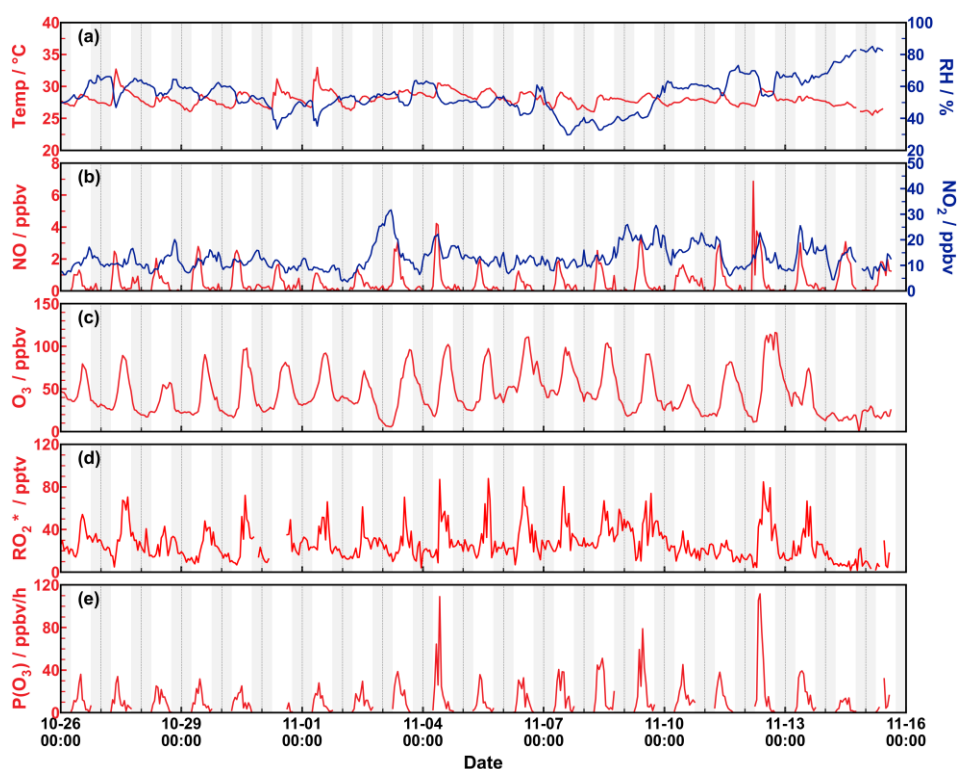


Figure 3. Time series of meteorological parameters (T, RH), major pollutants (O_3 , NO_x , RO_2^*), and daytime $\text{P}(\text{O}_3)$ (06:00–18:00) during the autumn observation period of 2024, with a temporal resolution of 1 hour.

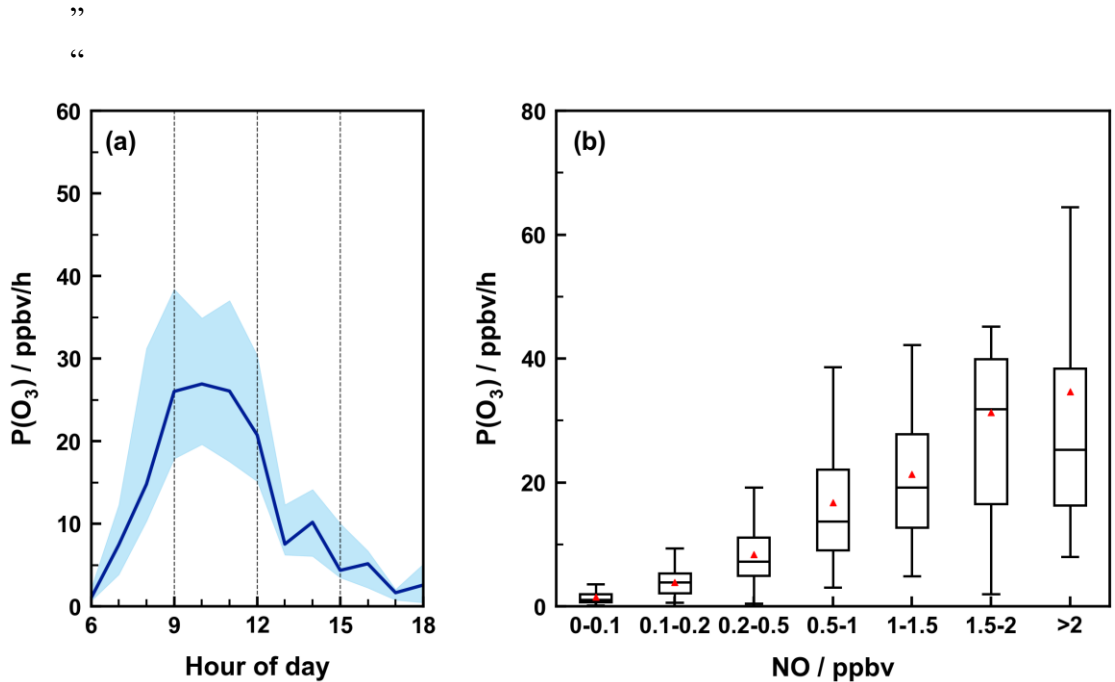


Figure 5. Diurnal variation and NO -dependent distribution of daytime $\text{P}(\text{O}_3)$. (a) Average diurnal profile of daytime $\text{P}(\text{O}_3)$ during the observation period. The dark line denotes the median, and the light blue shading indicates the interquartile range (25th–75th percentile). (b) Box plots of daytime $\text{P}(\text{O}_3)$ 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.

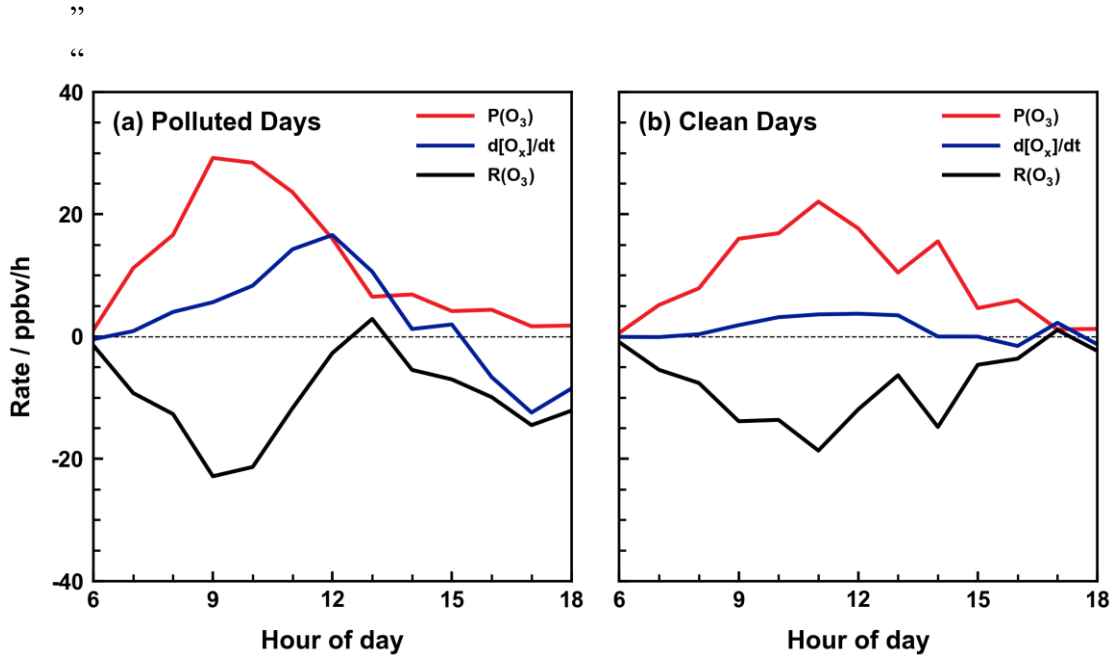


Figure 6. Diurnal variations of daytime $\text{P}(\text{O}_3)$, $d[\text{Ox}]/dt$, and $\text{R}(\text{O}_3)$ during (a) polluted and (b) clean periods. The red line represents the photochemical ozone production rate $\text{P}(\text{O}_3)$, the blue line indicates the rate of change of total oxidants $d[\text{Ox}]/dt$, 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](#)”.

REFERENCE

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Response to comments

Referee #2:

General comments: This manuscript presents the development of a compact PERCA–CEAS system for in situ measurements of total peroxy radicals (RO_2^), together with its application during a field campaign in Zhuhai. The topic is highly relevant for the atmospheric chemistry community, as direct measurements of peroxy radicals are essential for understanding ozone formation processes. The reported detection limit (~ 0.2 pptv) and successful field deployment demonstrate promising instrument performance.*

Overall, the manuscript contains valuable results; however, I believe that major revisions are required before publication. My main concerns relate to the description and validation of the measurement technique, particularly the chain length (CL) calibration, as well as some conceptual simplifications and inconsistencies in the instrument description. I also suggest improvements in clarity and language throughout the manuscript.

Response: Thank you for the valuable comments. We have fully considered your concerns, improved the chain length calibration experiment and clarified the instrument description throughout the manuscript. The detailed results are presented in our response letter. **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 [2-1]: **Definition and terminology of RO_2^* .** Lines 15 and 42: *It may be more precise to define RO_2^* as $HO_2 + \Sigma RO_2$, rather than $HO_2 + RO_2$. It would also be helpful to ensure consistent treatment of RO_2^* as a sum of radical species throughout the manuscript.*

Response [2-1]: Thank you for the suggestion. We have redefined RO_2^* as “ **$HO_2 + \Sigma RO_2$** ” in lines 15 and 42, and ensured consistent terminology throughout the manuscript.

Comment [2-2]: **Chain length (CL) calibration and radical interferences.** *The CL calibration described in Section 2.2 may introduce a systematic overestimation of CL. Photolysis of H_2O produces both OH and H radicals, which may introduce OH into the reactor. If OH reaches the inlet, it can participate in amplification (starting with R4) but is not accounted for in the S_2 signal.*

A possible validation approach would be to add sufficient CO in the HO_2 source to convert OH into HO_2 . Extra caution should be taken while adding CO to the source to avoid CL interference coming from the added CO triggering chain reaction in the background mode. It should also be acknowledged that PERCA systems amplify OH and RO radicals, which may become relevant during calibration conditions.

Response [2-2]: Thank you for pointing out this issue. To address the potential

systematic overestimation of CL caused by OH radicals, we redesigned the calibration setup. In this optimized configuration, CO (or N₂ for background mode), originally introduced at the front of the Nafion reactor, is premixed with synthetic air and then introduced immediately downstream of the H₂O photolysis zone, allowing rapid mixing with the photolysis products. This facilitates the prompt conversion of both OH and H radicals into HO₂, while minimizing potential wall losses of radicals before they enter the reactor. During the calibration, the total sampling flow rate and the concentrations of NO and CO within the Nafion reactor remained strictly consistent with our previous experimental conditions.

The revised calibration procedure and signal recording logic are as follows: When the mercury lamp is turned on, CO is introduced upstream in the amplification mode, ensuring that OH is quantitatively converted into HO₂. The total HO₂ concentration is twice that derived from H+O₂ pathway alone. The corresponding NO₂ signal is recorded as S₁, which represents the amplified NO₂ produced through the chain reaction initiated by this total HO₂. In the background mode with the lamp still on, N₂ is substituted for CO upstream. In the absence of CO within the reactor, the chain reaction is not triggered and only the HO₂ derived from H+O₂ pathway reacts with NO. The corresponding signal in this mode is recorded as S₂. Subsequently, when the mercury lamp is turned off, the NO₂ signals are recorded as S₃ and S₄ under the same amplification and background gas flow conditions, respectively. Consequently, the Chain Length is determined by the formula $CL = (S_1 - S_3) / [2 (S_2 - S_4)]$.

Using this revised procedure, we found that the overestimation of CL associated with OH-derived HO₂ is 47%, and the effective chain length is determined to be 30 ± 2 under our calibration conditions. Accordingly, we have updated the procedures described in Section 2.2 and revised the optimal CL results shown in Section 3.1.

Section 2.2:

“In this work, CL was determined using on-site peroxy radical calibration sources based on water vapor photolysis. A pen-type Hg lamp was used to photolyze H₂O in an N₂ carrier gas (mixture of dry and humidified N₂), producing H atoms and OH radicals (R5). Immediately downstream of the lamp, a mixture of synthetic air and reagent gases (CO/N₂ or CH₄/N₂) was introduced to allow rapid mixing with the photolysis products and reduce radical wall losses. In this configuration, H atoms react with O₂ in the synthetic air to form HO₂ (R6), while the reagent gases control the radical composition. When CO is used as the reagent gas, OH radicals are quantitatively converted to HO₂ (R4), providing a HO₂ calibration source without interference from OH and RO₂ radical.”

“The CL was determined using four distinct NO₂ signals detected by the CEAS. For the pure HO₂ source, the Hg lamp was switched on and CO was introduced immediately behind the H₂O photolysis zone, with NO at the inlet of Nafion reactor. Under these conditions, both H atoms and OH from H₂O photolysis were promptly converted to HO₂, then titrated by NO to form NO₂. The resulting NO₂ signal is denoted as S₁ (amplification mode). In the background mode, the lamp remained on while CO was substituted by N₂. The corresponding NO₂ signal, S₂, represents the background mode when HO₂ is only produced by H+O₂ pathway. With the lamp off, signal S₃ and

S_4 correspond to the amplification and background signals in the absence of radicals, respectively. Thus, $(S_2 - S_4)$ represents the HO_2 only produced by $H+O_2$ pathway, whereas $(S_1 - S_3)$ corresponds to the chain-amplified NO_2 signal from HO_2 produced via both the $H + O_2$ and $OH + CO$ pathways. The CL is then obtained from these four signals using Eq. (2).

$$CL = \frac{\Delta NO_2}{[HO_2]} = \frac{S_1 - S_3}{2(S_2 - S_4)} \quad (Eq. 2)$$

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Section 3.1:

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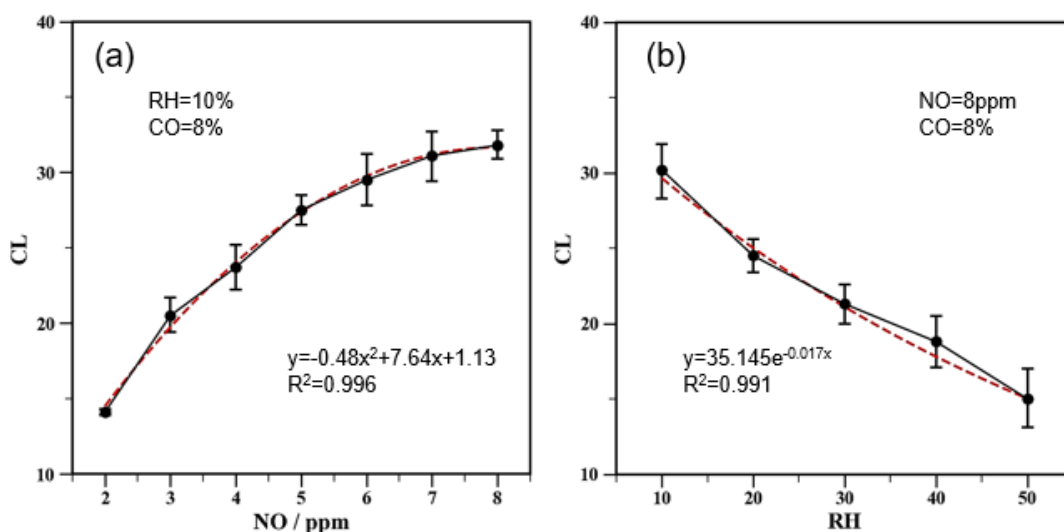


Figure 2. (a) Relationship between the CL and NO concentration under conditions of 10% RH and 8% CO concentration. (b) Variation of CL with RH at a fixed NO concentration of 8 ppm and CO concentration of 8%. (Error bars represent the standard deviation of five independent measurements.)

”

“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.”

Comment [2-3]: **Representativeness of CL for RO_2 species.** CL for RO_2 is generally lower than for HO_2 , and this difference depends strongly on system-specific factors such as wall losses and reactor design. Therefore, adopting uncertainties from other instruments (Kartal et al., 2010) may not be appropriate without justification. The authors should consider calibration with at least one RO_2 species or clearly state this as a limitation.

Response [2-3]: Thank you for the comment. We performed a dedicated calibration using methyl peroxy radicals (CH_3O_2) in addition to the standard HO_2 source. Specifically, a mixed HO_2 – CH_3O_2 calibration source was generated by replacing CO with CH_4 (150 ppm in N_2) immediately downstream of the H_2O photolysis zone. In this configuration, OH radicals react with CH_4 to form CH_3O_2 via $OH + CH_4 + O_2 + M \rightarrow CH_3O_2 + H_2O + M$, while H atoms are efficiently converted to HO_2 . The setup is

expected to yield a mixture of 50% HO₂ and 50% CH₃O₂. Our results show that the CL derived from this mixed source differs from that obtained using the pure HO₂ source by 20%, with a measured CL of 24.

These details have been added in Sections 2.2 and 3.1, and the resulting uncertainty has been incorporated into the overall uncertainty budget (Section 3.2).

Sections 2.2:

“...RO₂ radical. When CH₄ (150 ppm in N₂) is used instead of CO, OH reacts with CH₄ to form CH₃O₂ (R7), yielding a mixed peroxy radical source containing approximately 50 % HO₂ and 50 % CH₃O₂ under typical calibration conditions.”

“...using Eq. (2). The mixed HO₂–CH₃O₂ standard was generated by introducing CH₄ only during the S₁ (amplification) measurement and was used to verify the instrument response to organic peroxy radicals relative to HO₂ under otherwise identical conditions.”

Sections 3.1:

“...HO₂ calibration. Calibration using a mixed radical source consisting of 50% HO₂ and 50% CH₃O₂ yielded a CL of 24±1 under the same conditions.”

Sections 3.2:

“(3) Uncertainty in radical partitioning. This arises from variability in the relative contributions of HO₂ and CH₃O₂ to total peroxy radicals. Based on the reported HO₂/RO₂ (0.8–1.2) and CH₃O₂/RO₂ (0.85–0.95) ratios from Stone et al., (2010), the mole fraction of CH₃O₂ in total peroxy radicals (f) is estimated to be 0.41–0.54. Under these conditions, the use of an HO₂-based calibration would introduce a systematic bias of 16–22% in the derived RO₂* concentration.”

Comment [2-4]: **Instrument description.** *As this is the first publication of the PWRC system used, additional details such as flow rate, residence time, reactor pressure, detector flow conditions, etc should be included for reproducibility.*

Response [2-4]: Thanks for the suggestions. We have clarified additional details of technical specifications in Section 2.1, such as reagent gas purities, flow rates, mixing ratios, reactor dimensions, and residence times. The revised text is as follows:

“The NO and CO gases were injected into the system accompanied by N₂ as a balancing gas. To ensure gas purity, the NO (100 ppmv in N₂) was passed through a ferrous sulfate heptahydrate (FeSO₄·7H₂O) filter to remove trace NO₂ impurities. The flow rate of this NO mixture was regulated at 120 mL/min, achieving a final concentration of 8 ppmv in the reactor. Similarly, high-purity CO gas (99.99%) was passed through an activated carbon column to eliminate residual carbonyl compounds before entering the reactor at 120 mL/min, corresponding to a constant concentration of 8% (v/v) during amplification mode. The total system flow was maintained at 1500 mL/min using mass flow controllers, corresponding to a residence time of approximately 3 s in the reaction zone.”

Comment [2-5]: **Valve configuration.** *There is inconsistency between the text and schematic regarding valve configuration.*

- Line 156 refers to one three-way solenoid valve,

- Figure 1 shows four two-way valves
- Line 160 also mentions four solenoid valves.

This should be clarified.

Response [2-5]: Thanks for the careful check of the valve configuration. We apologize for the inconsistency in the description of the valve configuration. The system actually uses four two-way solenoid valves instead of three-way valves. The text has now been revised to ensure consistency with Figure 1. We have updated the description in Section 2.1 to explicitly state this configuration.

“To enable automated switching between amplification and background modes in the single-channel configuration, an automatic valve-switching module driven by a programmable timer was developed. The flow paths of CO and N₂ were controlled using four two-way solenoid valves, with two valves assigned to each gas line. During the amplification mode, the timer directs CO to the front inlet to initiate the chain reaction with NO, while N₂ is routed to the rear inlet. Conversely, in the background mode, the valve states are toggled so that N₂ is introduced at the front and CO is directed to the rear. By synchronizing the switching of these four valves, the system achieves stable and automated mode transitions for real-time detection of peroxy radicals.”

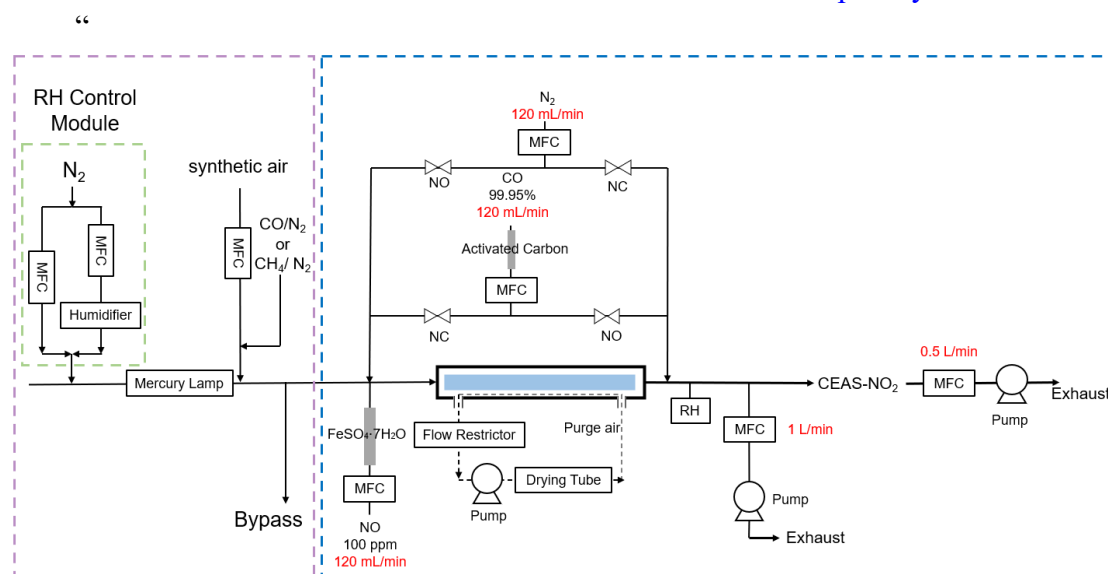


Figure 1. Schematic diagram of the PERCA-CEAS system. The purple dash line portion represents the standard source module, which consists of the standard gas generation unit and the relative humidity (RH) control unit (outlined in green) and is used for calibrating the system chain length. The blue dash line portion represents the measurement module, comprising the chemical amplification unit and the NO₂ detection unit, which together enable the quantification of atmospheric peroxy radicals.

Comment [2-6]: HO₂ source in the schematic diagram. The schematic suggests N₂ is humidified prior to photolysis, but HO₂ formation requires O₂. The authors should clarify how O₂ or synthetic air is introduced and whether it is always present. The

Modeling) under the experimental conditions (26.5 °C and 3 s residence time). The simulations indicate that the chemical amplification process is highly time-limited, reaching near completion within approximately 0.15 s. Within this short reaction window, only a fraction of PAN-derived radicals can effectively participate in the chain propagation before being removed by wall losses or exiting the reaction zone. Importantly, any NO₂ produced from slower PAN thermal decomposition outside the effective reaction window is also present in both amplification and background modes and is therefore removed through the differential measurement approach. Under a representative PAN level of 1.0 ppbv, the interference generated within the effective reaction window corresponds to an equivalent RO₂* signal of ~1.95 pptv. This accounts for approximately 1.3–9.8% of the typical RO₂* concentrations (20–150 pptv) observed during the campaign and has been incorporated into the overall measurement uncertainty.

We have added a detailed discussion regarding the potential interference from PAN thermal decomposition in Section 3.2 of the revised manuscript.

“(4) PAN interference. The thermal decomposition of PAN represents a potential source of interference, as it releases NO₂ and peroxy radicals that can trigger additional chemical amplification within the reactor (Liu and Zhang, 2014; Wood and Charest, 2014). Kinetic simulations using the F0AM model (Framework for 0-D Modeling; Wolfe et al., 2016) indicate that 1.0 ppbv PAN results in an equivalent RO₂* signal of 1.95 pptv under our experimental conditions (26.5 °C and a amplification reaction time of 0.15 s). This accounts for 1.3–9.8% of the typical RO₂* levels (20–150 pptv) observed during the campaign.”

Comment [2-8]: **Interpretation of chain length comparisons.** *CL comparisons should consider reactor material, reactor design, working pressure, humidity, and wall losses. Instruments such as Horstjann et al., (2014) include pre-reactor chambers that increase wall losses. The comment about influence of detection technique on CL should be reconsidered.*

Response [2-8]: Thanks for the suggestion. To address this, we have revised Section 3.1 and added Table 1 to provide a detailed summary of calibration conditions and technical specifications for previous PERCA systems.

“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 (George et al., 2020; Wood and Charest, 2014). The differences in CL are primarily attributed to wall loss of HO₂ radicals due to reactor material, reactor design and working pressure. Although the obtained CL is relatively low compared with these PERCA instruments, our results demonstrate that the developed PERCA-CEAS system provides stable and reliable sensitivity for atmospheric RO₂* measurements.

Table 1. Summary of performance for reported PERCA measurement systems

Measurement System	Channel Configuration	Calibration Source	CL	LOD	Uncertainty	Pressure (mbar)	Reference
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PERCA-luminol	Single	CH ₃ O ₂	200-260	2 pptv	40%	400 ~ 1000	(Green et al., 2003)
PERCA-luminol	Dual	HO ₂ 50%HO ₂ +50%CH ₃ O ₂	45±7	3±2 pptv (3σ)	/	200	(Kartal et al., 2010)
PERCA-luminol	Dual	HO ₂ 50%HO ₂ +50%CH ₃ O 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 ₃ O ₂	200 180	4 pptv (3σ)	/	1000	(Liu and Zhang, 2014)
PERCA-CRDS	Dual	HO ₂ 50%HO ₂ +50%CH ₃ O 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 ₃ C(O)O ₂ CH ₃ O ₂	168±20	0.6 pptv (1σ, 60s)	25%	1000	(Wood and Charest, 2014)
ECHAMP-CAPS	Dual	CH ₃ C(O)O ₂ CH ₃ O 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 ₃ O ₂	30±2 24±1	0.38 pptv (1σ)	18.4-25.7%	1000	This work

”

Comment [2-9]: ***Simplifications in ozone production analysis.*** The assumption $k_{eff} = k(HO_2+NO)$ and simplified $D(O_3)$ estimates should be discussed as sources of uncertainty.

Response [2-9]: Thanks for the suggestion. Considering the uncertainties associated with RO₂* measurements (18.4-25.7%), the k_{eff} approximation (~10%) and the upper limit of D(O₃) level (5%), the overall uncertainty in P(O₃)_{net} is estimated to be 21.5-28.0% according to error propagation calculation. These uncertainty analyses have been added to the revised text in Section 3.4.

“Considering uncertainties associated with RO₂* measurements (18.4-25.7%), the approximation of k_{eff} (~10%), and the upper limit of D(O₃) level (5%), the overall uncertainty in P(O₃)_{net} was estimated to be 21.5-28.0%.”

Comment [2-10]: **Interpretation of VOC influence.** *The attribution to VOC reactivity in Line 326 requires supporting evidence or should be presented more cautiously.*

Response [2-10]: Thanks for the suggestion. Although in-situ VOC measurements were not conducted, regional studies suggest relatively high VOC reactivity in the study area. Studies at nearby coastal sites (e.g., Da Wan Shan Island) have reported high oxidative capacity in air masses over the Pearl River Estuary, associated with strong VOC consumption and enhanced radical cycling (Sun et al., 2024). In addition, the subtropical climate and dense vegetation in the Pearl River Delta contribute substantial biogenic emissions (e.g., isoprene), which may enhance the regional radical budget (Situ et al., 2013; Wang et al., 2023c). At our site, these elevated VOC levels are likely to sustain RO₂ formation and reduce sensitivity to NO titration, thereby shifting the RO₂*- NO transition toward higher NO levels. We have strengthened the discussion by adding supporting literature on VOC reactivity in Section 3.3 of the revised manuscript.

“This behavior is consistent with the elevated VOC reactivity inferred for studies conducted near our observation site. Studies at nearby coastal sites (e.g., Da Wan Shan Island) have reported high oxidative capacity associated with strong VOC consumption and enhanced radical cycling (Sun et al., 2024), while the dense vegetation in the Pearl River Delta contributes substantial biogenic VOC emissions (e.g., isoprene) (Situ et al., 2013; Wang et al., 2023c). Collectively, these factors contribute to sustaining propagation cycles of RO₂ radical and shift the turning point of the NO dependence of RO₂* concentration higher at our site.”

Comment [2-11]: **Interpretation nighttime RO₂*.** *If the nighttime RO₂* is attributed to NO₃ driven chemistry, more detailed scientific explanation is necessary since NO₃ measurement are not given.*

Response [2-11]: Thanks for the suggestion. To provide further clarification, the nitrate radical production rate, P(NO₃), was calculated as follows:

$$P(NO_3) = k[NO_2][O_3]$$

where $k_{NO_2+O_3}$ represents the temperature-dependent rate constant for the reaction between NO₂ and O₃ (Atkinson et al., 2004). During the campaign, the average nighttime (18:00–06:00) P(NO₃) was approximately 1.4 ppbv·h⁻¹, higher than the reported warm-season mean of 1.07 ± 0.38 ppbv·h⁻¹ over China (Wang et al., 2023a), indicating active nighttime NO₃ chemistry at this site. This substantial production rate suggests the presence of an efficient nighttime oxidation pathway and helps explain the observed RO₂* levels. We have added this quantitative analysis and a more detailed discussion of NO₃ chemistry to Section 3.3 of the revised manuscript.

“... at night (Figure 4a). The relatively high level of RO₂* at night indicates the presence of a nighttime peroxy radical source possibly due to NO₃ chemistry oxidation. We found that the average NO₃ production rate (P(NO₃)) at night during the campaign was approximately 1.4 ppbv·h⁻¹, higher than the reported warm-season mean of 1.07 ± 0.38 ppbv·h⁻¹ over China (Wang et al., 2023a), indicating active nighttime NO₃ chemistry at this site.”

Minor Comments

Line 76: wording correction.

Thank you for the suggestion. The wording has been revised to “NO and CO are introduced to drive chain reactions that amplify peroxy radicals into detectable NO₂ signals.”

Line 264: extra space.

Corrected accordingly.

Line 275: define abbreviations and use LOD.

Corrected accordingly.

Line 313: 'deceased' should be 'decreased'. O₃ range appears reversed.

Corrected accordingly.

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