

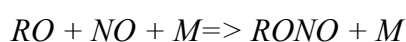
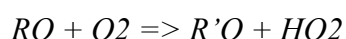
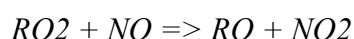
**Response to Reviewers' Comments on Manuscript ID egosphere-2024-3210:
"Observation and modelling of atmospheric OH and HO₂ radicals at a
subtropical rural site and implications for secondary pollutants"**

We sincerely appreciate the editor and the three referees for thoughtful comments and valuable suggestions which has helped us to improve our manuscript. In response to your comments, we have undertaken a comprehensive revision of the manuscript.

Please find our itemized responses below and revisions in the re-submitted files. We use *italicized* text for your questions, **blue** for our response, and **red** to indicate where changes have been made in the manuscript. The changes inside the manuscript will be highlighted **in yellow**.

Reviewer 3

The manuscript reports about CIMS measurements of OH and HO₂ in a subtropical rural site and the comparison of them with the results of MCM box model. Although in general simultaneous measurements of OH and HO₂ provide very helpful information for understanding of radical budgets and the article reporting such measurements would potentially be of an interest, the present study cannot be published in its present form because it actually does not report HO₂ measurements. The method used in this study for detection of peroxy radicals by their conversion to OH in reaction with added NO will result in about the same conversion efficiency for both HO₂ and organic peroxy radicals RO₂. To distinguish between the HO₂ and RO₂ radicals using the conversion scheme with NO several groups previously developed CIMS methods based on a modulation of chemical conditions in their instruments to measure either HO₂ or RO₂, predominantly (Hanke et al., 2002; Edwards et al., 2003; Hornbrook et al., 2011). In brief, HO₂ mode requires efficient suppression of RO₂ to HO₂ conversion in reaction of alkoxy (RO) radicals with O₂ in favor of the formation of alkyl nitrites:



Although the authors of the present manuscript make reference to the study of Edwards et al., 2003, they use NO concentration of 1.2 ppm leading to about 90% conversion of RO to HO₂ and resulting in similar contribution of HO₂ and RO₂ to the detected signal, assuming their similar ambient concentrations. Referring in the manuscript supplement to the study of Fuchs, 2014 as an example of using the same NO concentration of 1.2 ppm for HO₂ detection the authors do not take into account low pressure in the FAGE conversion stage, hence low O₂, making RO+O₂ reaction negligible and allowing HO₂ measurements with low interference from RO₂, although not for all of RO₂ (Fuchs et al., 2011). Finally, the authors do mention once "interference" from RO₂ by saying that "To access HO₂ interference caused by the ambient RO₂ conversion, the model underwent a three-days spins-up to simulate the ambient RO₂ concentration". However, it doesn't seem to be a correct procedure to make correction using the model and after

that compare the measurements corrected in this way with the same model.

The present OH and “HO₂” measurements may still be of value and present the basis of an important publication. However, for this the measurements should be correctly interpreted and presented with detailed description of a calibration procedure of the peroxy radicals.

Response: Thank you for your insightful comment. In our study, both the experimental and modelling results did not show significant RO₂ interference under our environmental conditions. Therefore, we consider our measurements to be representative of ambient HO₂ concentration.

The details were added to the revised manuscript on page 7:

“Interference from RO₂ can affect HO₂ measurements, potentially resulting in an overestimation of ambient HO₂ levels (Edwards et al., 2003; Fuchs et al., 2014; Hanke et al., 2002). In our study, both the experimental and modelling results did not show significant interference under our environmental conditions (Text S4.3).”

The contents were added an Text S4.3 on page 11 on SI as below:

“To assess the possible HO₂ interference from RO₂, we first simulated with a box model production of HO₂ from RO₂ in the inlet system with addition of 1.2 ppm NO to ambient air composition observed in previous field study in Hok Tsui (a coastal site in Hong Kong) by our team in 2020 (Zou et al., 2023) before this observation. The observation-constrained MCM model (described in the Text S6) was run for three days, and the RO₂ outputs were taken as used as the initial concentrations entering the inlet. Then another model run was conducted by setting j-values setting to zero and reaction time as the residence time (47 ms) to simulate the conversion of RO₂ by NO in the CIMS inlet. We compared the OH concentrations (from RO₂ conversion to HO₂ and then to OH) at the outlet with the total concentration of HO₂+OH after spinning up. The result shows a difference of less than 2% suggesting negligible conversation of RO₂ to HO₂ in the inlet at 1.2 ppm NO injection. Similar model tests with real time conditions were also done for Conghua study after field study and show less than 2% interference.

To verify the model results, experiment tests were conducted in both laboratory and field settings (Hok Tsui in Hong Kong and Conghua) by comparing the HO₂ calibration factor obtained in synthetic air (with minimal interference of RO₂ due to very low VOCs concentrations in the synthetic air) and that conducted in indoor and outdoor air (with potential interference due to presence of VOCs). The results in Table S6 show difference of 1% - 3% between the HO₂ calibration factor in the synthetic air with that in the lab indoor air and that in the ambient air at Hok Tsui (with [O₃] <70 ppb [NO_x] < 10 ppb) as well as Cong Hua (with [O₃] <60 ppb [NO_x] < 10 ppb), confirming little interference of RO₂ to HO₂ measurements (See Table S6 below). These results might be due to the low concentrations of biogenic volatile organic compounds (BVOCs) in our two study sites ([C₅H₈] <0.2 ppb) as previous studies show large interference of BVOC than anthropogenic VOC to HO₂ measurements (Fuchs et al., 2014).

Table S5 Calibration factors of OH and HO₂ obtained in different conditions to estimate the RO₂ interference.

Year of experiments	Calibration Conditions	Calibration Factor (cm ³)		Notes
		OH	HO ₂	
2021	Synthetic air in lab	7.912E-10	9.156E-10	On the afternoon of
	Indoor air in lab	8.146E-10	9.275E-10	<u>Nov 20, 2021</u>
	Synthetic air at Hok Tsui	8.212E-10	9.181E-10	On the morning of
	Outdoor air at Hok Tsui	8.252E-10	9.378E-10	<u>Dec 23, 2021</u>
2022	Synthetic air in lab	1.043E-09	1.080E-09	On the morning of
	Indoor air in lab	1.035E-09	1.119E-09	<u>May 04, 2022</u>
	Synthetic air at Conghua	1.033E-09	1.085E-09	On the morning of
	Outdoor air at Conghua	1.025E-09	1.092E-09	<u>Nov 17, 2022</u>

Notes:

The difference between calibration factors obtained at 2022 and 2020 is due to the changes of CIMS's settings

Chemical Condition of outdoor air of Hok Tsui [O₃] <70 ppb, [NO_x] < 10 ppb, [C₅H₈] < 0.2 ppb

Chemical Condition of outdoor air of Cong Hua [O₃] <60 ppb, [NO_x] < 10 ppb, C₅H₈ < 0.2 ppb

”

As to the referee's comment on our correction of interference by comparing model and observations, the correction affected concentrations of less than 2%. We agree with the referee that this correction is take account for partial interference. However, the small correction is consistent with the test results shown above indicating minimal interference of RO₂ to HO₂ during the field study.

The following modification have been made on page 14 of SI as below:

“Text S6 The model efforts to correct measurement interference.

Ambient NO can cause interference to OH measurement by concerting HO₂ to OH in the inlet system. To assess and correct this effect, model simulations were conducted, which also simulated conversion of RO₂ to HO₂ by NO (i.e., interference to HO₂ measurements as discussed before). We first constrained all measured species (except OH and HO₂) in the model, and a three-day spin-up was used to simulate the chemical conditions of the sampled air during measurement. Then the outputs were used as inputs for another simulation with the injection gases (SO₂ and/or NO) to simulate chemical reactions in the inlet with reaction time of 47 ms to match the reaction time in the CIMS. Photolysis frequencies were maintained at zero to reflect the dark environment of the inlet. The modeled OH concentrations without NO addition and OH concentrations with NO addition represent ambient NO interference to OH and HO₂, respectively.

The calculated interferences for OH and HO₂ measurements were in the range 1×10⁴ cm⁻³ to 1×10⁵ cm⁻³ (mean: 3×10⁴) and 8×10⁵ cm⁻³ to 2×10⁶ cm⁻³ (mean: 1.2×10⁶), respectively. These lead to correction of measurement data of OH and HO₂ less than 2%.”