We sincerely thank the reviewer for the thoughtful and detailed comments provided in this third round of review. We carefully considered each suggestion and revised the manuscript accordingly. In the response below, we use *italic font* to represent the reviewer's comments, **blue text** for our replies, and **red text** to quote content directly from the revised manuscript. Specific revisions are highlighted in **yellow** within the marked-up manuscript for clarity.

I suggest to replace "HO2" by something similar to what was previously used to denote HO2+RO2 in numerous publications reporting peroxy radical measurements made with CIMS or PERCA, e.g. "sum of peroxy radicals". The "HO2*" notation is not common, although it was used in the body of a few publications reporting HO2 measurements with FAGE.*

Thank you for the suggestion. Our instrument configuration during the field study did not measure all RO_2 radicals but a portion of them. So, the term "$HO_2 + RO_2$" or "sum of peroxy radicals are not suitable to our measurement. We would like to retain "HO_2*" to represent the positively biased HO_2, which is analogous to the use of the term NO_2* for positively biased NO_2 measured using a thermal catalytic conversion method. Using HO_2* is also in line with its uses in recent publications.

Abstract

1. *p.1 l.19. "(HO2 + parts of RO2)" I think, better to say HO2 + contribution from RO2. Also define here the "RO2".*

   Thanks for the suggestions. We agree and have made the suggested revision as shown below:

   "This study measured HO_2* (HO_2 + contribution from RO_2, organic peroxyl radicals) and OH concentrations……"

2. *p.1, l.22-23. "Model estimated interference to HO2 by RO2 possibly contributed to 44%-69% of the HO2*".Is it rather estimated contribution from RO2 to HO2* during the measurements period, ranging from 44% to 69%? Please reformulate.*

   To improve clarity, the sentence has been updated accordingly:

   "Model estimated contribution from RO_2 to HO_2 during the measurement period ranged from 44% to 69% of the HO_2*."

Introduction

3. *p.2,l.9. "where R represents an alkyl group" There are many types of peroxy radicals, not just alkyl peroxy radicals!*

   Thanks for pointing this out. We have revised the text and the change is provided below:

   "……producing HO_2 and other organic peroxyl radicals (RO_2, where R represents an organic group such as alkyl, acyl, or aryl)."

4. *p.2,l.15. Define HOx*

   The definition of HO_x was added as shown below:

   "HO_X ($OH + HO_2$) radicals are removed……"

5. *p.3,l.26. Define "HO2*" used here for the first time.*

   The definition of HO_2* was added as shown below:

   "……concentrations of OH and HO_2* (HO_2 + contribution from RO_2) using……"

Methodology

6. *p.4, l.25. Add information about HCHO to the Tables S2 and S4*

   Thank you. The measurement method and values for HCHO photolysis and other species (J

values) have been added to Tables S2 and S4 as shown below:

Table S2:

Instruments	Species	Resolution	Detection Limits	Accuracy
Q-CIMS (NO_3^-)	OH	1 hours	3×10^5 cm^{-3}	± 46%
	HO_2*	1 hours	20×10^5 cm^{-3}	± 44%
Thermo 42i-TL	NO	1 min	60 ppt	± 5.2%
Thermo 49i	O_3	1 min	1 ppb	± 6.0%
NO_2-11r-EP	NO_2	1 min	60 ppt	± 6.0%
Online GC-MS	VOCs	1 hour	10 ppt	± 20%
Thermo 43i	SO_2	1 min	0.5 ppb	± 6.1%
Thermo 48i	CO	1 min	40 ppb	± 7.4%
Thermo 17i	NH_3	2 mins	1 ppb	± 8%
LOPAP-03	HONO	5 mins	1 ppt	± 10%
APR-1000	Photolysis Frequencies	1 mins	1×10^{-8} s^{-1}	± 5%
SMPS	Aerosol Particles	5 mins	1 particle cm^{-3}	± 10%

Table S4:

Species	Total	PRD	CEC	CNC	MCM Abb.
Ethane	2.301±0.826	1.613±0.883	1.864±0.534	2.032±0.141	C2H6
Ethylene	0.691±0.331	0.622±0.257	0.582±0.206	0.581±0.162	C2H4
Propane	1.593±0.618	2.099±0.808	1.217±0.314	1.239±0.274	C3H8
Propene	0.072±0.077	0.127±0.173	0.059±0.023	0.067±0.035	C3H6
i-Butane	0.439±0.281	0.891±0.494	0.353±0.103	0.310±0.061	IC4H10
n-Butane	0.653±0.405	1.284±0.709	0.484±0.145	0.438±0.083	NC4H10
Acetylene	0.917±0.416	0.905±0.350	0.819±0.305	0.758±0.072	C2H2
trans-2-Butene	0.015±0.007	0.015±0.005	0.017±0.011	0.016±0.006	TBUT2ENE
cis-2-Butene	0.083±0.038	0.165±0.033	0.083±0.013	0.080±0.014	CBUT2ENE
Butene	0.044±0.021	0.047±0.049	0.037±0.014	0.048±0.010	BUT1ENE
Chloromethane	0.838±0.221	0.510±0.076	0.839±0.153	0.856±0.154	CH3CL
1,3-Butadiene	0.008±0.008	0.012±0.009	0.008±0.007	0.007±0.005	C4H6
Acetaldehyde	0.922±0.355	1.456±0.365	NaN	0.525±0.160	CH3CHO
Bromomethane	0.009±0.002	0.010±0.002	0.009±0.001	0.009±0.001	CH3BR
Chloroethane	0.023±0.012	0.015±0.011	0.021±0.009	0.020±0.004	CH3CH2CL
i-Pentane	0.338±0.167	0.610±0.224	0.311±0.059	0.237±0.042	IC5H12
1-Pentene	0.043±0.016	0.067±0.024	0.033±0.008	0.037±0.006	PENT1ENE
n-Pentane	0.187±0.102	0.339±0.181	0.121±0.034	0.136±0.022	NC5H12
trans-2-Pentene	0.003±0.005	0.011±0.005	0.002±0.002	0.001±0.001	TPENT2ENE
cis-2-Pentene	0.002±0.003	0.007±0.003	0.001±0.001	0.000±0.001	CPENT2ENE
Acrolein	0.060±0.031	0.092±0.043	0.053±0.019	0.043±0.015	ACR
Propanal	0.011±0.006	0.015±0.011	0.010±0.004	0.009±0.004	C2H5CHO
Vinylidene chloride	0.004±0.003	0.003±0.002	0.002±0.002	0.005±0.003	CCL2CH2
2,2-Dimethylbutane	0.017±0.015	0.046±0.025	0.012±0.003	0.010±0.002	M22C4
Dichloromethane	1.142±0.838	2.510±1.430	1.035±0.347	0.933±0.179	CH2CL2
2,3-Dimethylbutane	0.026±0.023	0.064±0.033	0.025±0.007	0.015±0.004	M23C4
2-Methylpentane	0.071±0.045	0.237±0.053	0.060±0.016	0.056±0.012	M2PE
3-Methylpentane	0.052±0.039	0.120±0.061	0.040±0.011	0.036±0.009	M3PE
Methyl tert-butyl ether	0.072±0.042	0.135±0.051	0.068±0.016	0.055±0.012	MTBE
1-Hexene	0.005±0.005	0.013±0.004	0.004±0.004	0.002±0.001	HEX1ENE
n-Hexane	0.066±0.043	0.131±0.063	0.049±0.016	0.042±0.012	NC6H14
Methacrolein	0.062±0.062	0.116±0.058	0.108±0.069	0.025±0.010	MACR
1,1-Dichloroethane	0.009±0.005	0.008±0.004	0.008±0.004	0.007±0.001	CHCL2CH3
Butyraldehyde	0.536±0.211	0.446±0.179	0.496±0.142	0.448±0.157	C3H7CHO
1,2-Dichloroethylene	0.049±0.076	0.138±0.171	0.032±0.014	0.026±0.014	DICLETH
2-Butanone	0.248±0.244	0.546±0.490	0.214±0.086	0.134±0.050	MEK
Ethyl acetate	0.267±0.386	0.707±0.868	0.174±0.076	0.148±0.076	ETHACET
Chloroform	0.082±0.032	0.125±0.042	0.087±0.015	0.069±0.010	CHCL3
Methylchloroform	0.002±0.001	0.004±0.000	0.001±0.000	0.002±0.000	CH3CCL3
2-Methylhexane	0.015±0.017	0.046±0.028	0.010±0.004	0.007±0.002	M2HEX
Cyclohexane	0.019±0.015	0.041±0.021	0.011±0.005	0.011±0.004	CHEX
Tetrachloromethane	0.073±0.006	0.070±0.004	0.066±0.004	0.075±0.003	CCL4
3-Methylhexane	0.020±0.024	0.064±0.042	0.012±0.004	0.009±0.003	M3HEX
Benzene	0.346±0.139	0.288±0.106	0.315±0.102	0.311±0.029	BENZENE
Ethylene dichloride	0.359±0.170	0.259±0.112	0.342±0.185	0.414±0.097	CH2CLCH2CL
n-Hepane	0.035±0.023	0.072±0.038	0.024±0.005	0.022±0.003	NC7H16
Crotonaldehyde	0.446±0.139	0.464±0.008	0.480±0.007	0.501±0.008	C3MDBAL
Trichloroethene	0.021±0.023	0.061±0.037	0.018±0.013	0.013±0.003	TRICLETH
1,2-Dichloropropane	0.085±0.038	0.118±0.030	0.096±0.016	0.071±0.011	CL12PROP
Pantanal	0.018±0.011	0.033±0.017	0.019±0.008	0.013±0.006	C4H9CHO
1,3-Dichloro-1-propene	0.003±0.001	0.003±0.001	0.002±0.001	0.002±0.001	CLC3H4CL
4-Methyl-2-pentanone	0.005±0.007	0.019±0.004	0.001±0.001	0.000±0.001	MIBK
Toluene	0.282±0.266	0.706±0.498	0.212±0.057	0.173±0.049	TOLUENE
n-Octane	0.009±0.007	0.022±0.007	0.005±0.001	0.005±0.001	NC8H18
1,1,2-Trichloroethane	0.014±0.010	0.011±0.008	0.013±0.009	0.015±0.005	CH2CLCHCL2
Tetrachloroethylene	0.015±0.013	0.040±0.019	0.014±0.004	0.009±0.001	TCE
2-Hexanone	0.050±0.025	0.087±0.029	NaN	0.038±0.011	HEX2ONE
Hexanal	0.041±0.022	0.076±0.025	NaN	0.030±0.009	C5H11CHO
1,2-Dibromoethane	0.002±0.002	0.004±0.001	0.001±0.001	0.002±0.001	DIBRET
Ethylbenzene	0.042±0.031	0.072±0.035	0.028±0.022	0.034±0.023	EBENZ
o-Xylene	0.039±0.030	0.077±0.039	0.027±0.018	0.031±0.017	OXYL
Styrene	0.020±0.013	0.034±0.008	0.012±0.005	0.013±0.007	STYRENE
Isopropylbenzene	0.006±0.006	0.016±0.003	0.003±0.001	0.003±0.001	IPBENZ
1,1,2,2-Tetrachloroethane	0.003±0.002	0.005±0.001	0.003±0.002	0.002±0.001	CHCL2CHCL2
n-Propylbenzene	0.005±0.004	0.013±0.003	0.003±0.001	0.002±0.001	PBENZ
m-Ethyltoluene	0.007±0.007	0.019±0.008	0.006±0.003	0.004±0.002	METHTOL
p-Ethyltoluene	0.005±0.005	0.013±0.005	0.003±0.002	0.002±0.002	PETHTOL
1,3,5-Trimethylbenzene	0.005±0.005	0.015±0.005	0.004±0.002	0.002±0.001	TM135B
n-Decane	0.003±0.003	0.009±0.003	0.002±0.001	0.001±0.001	NC10H22
Benzaldehyde	0.005±0.004	0.013±0.004	0.003±0.001	0.002±0.001	BENZAL
1,2,4-Trimethylbenzene	0.009±0.009	0.024±0.013	0.008±0.003	0.004±0.002	TM124B
1,2,3-Trimethylbenzene	0.004±0.003	0.010±0.004	0.003±0.002	0.002±0.001	TM123B
Undecane	0.002±0.002	0.006±0.001	0.002±0.001	0.000±0.001	NC11H24
Dodecane	0.009±0.003	0.015±0.003	0.007±0.001	0.010±0.002	NC12H26
j_{NO2} 10^{-3} (s^{-1})	1.3±1.9	1.3±2.1	1.4±2.0	1.6±2.3	J4
$j_{NO3\,M}$ 10^{-3} (s^{-1})	4.0±6.4	4.2±6.8	4.3±6.7	5.3±7.9	J5
$j_{HCHO\,M}$ 10^{-6} (s^{-1})	5.2±7.9	5.5±8.5	5.6±8.3	6.4±9.5	J9
$j_{HCHO\,R}$ 10^{-6} (s^{-1})	4.2±6.6	4.5±7.1	4.6±7.0	5.3±8.0	J10
j_{HONO} 10^{-3}(s^{-1})	0.2±0.3	0.2±0.4	0.2±0.3	0.3±0.4	J7
j_{H2O2} 10^{-6}(s^{-1})	1.0±1.5	1.0±1.6	1.1±1.6	1.2±1.8	J3

7. *p.5,l.6. Replace "HO2" by "HO2+RO2" or "HO2*". The same for many other HO2 occurrences.*

   We have replaced "HO_2" with "HO_2*" at this location and throughout the manuscript wherever it refers to the measured HO_2 * values.

8. *p.7,l.18. "79% or 222%" Use the same way and numbers to present RO2 contribution (compare with given here and in the Abstract).*

   We have changed the description of RO_2-contributed interference for consistency as follows: "For our CIMS configuration, the model estimated daytime interference from RO_2 ranged from 44% to 69% of the HO_2* during the field study (Text S4.3 and Figure S9)."

9. *p.8, l.1-3.*

   1) Make the reported here calibration coefficients consistent with presented in Table S3;

   2) For HO2 calibration it could be 46%, but for HO2 it is up to 222% (see above)*

3) How the background corresponding to H2SO4 mode was measured? As neither H2SO4 measurements nor H2SO4 calibration are presented here, the information about H2SO4 can be removed.

We thank the reviewer for the suggestions. The reported calibration coefficients in the main text have been revised for consistency with Table S3. We also corrected the uncertainty of HO_2* to reflect model-estimated RO_2 interference, and removed the mention of H_2SO_4 background and calibration, as these data are not presented in the manuscript.

"The calibration factors, detection limits and uncertainties were 1.09×10^{-8} cm^{-3}, 3×10^5 cm^{-3}, and 44% for OH; 1.07×10^{-8} cm^{-3}, 2×10^6 cm^{-3}, and 222% for HO_2^*, respectively (Table S3). The large uncertainty in HO_2* reflects the possible contribution of RO_2 interference, as discussed above."

Table S3 was also revised as below:

a) Hok Tsui 2020

Efficiency	Parameter	Gas	Values	Units	Specification for Measurement	Values	Units
E_{Conv}	Front Injection	SO_2 (0.9%)	5	sccm	Sample Flow [SO_2]	12	ppm
	Pulse Valve	N_2	2	sccm	Cycle Duration (OH)	6	mins
		C_3F_6 (99.9%	2	sccm	B/S Ratio for OH measurement	8%	
	Rear Injection	C_3F_6 (99.9%	2	sccm	Sample Flow [C_3F_6]	1072	ppm
		HNO_3	10	sccm	Reaction Time	47	ms
	Sample Flow		3.7	slpm	Sample Flow Speed	55	cm/s
E_{Ion}	Sheath Flow	Zero Air	12.6	slpm	Reynolds Number in Ionization Chamber	>4000 Turbulent flows	
		HNO_3	10	sccm			
		C_3F_6 (99.9%	2	sccm	Sheath Flow [C_3F_6]	159	ppm
	Total Flow		16.8	slpm	Sheath Flow Speed	25	cm/s
	Sheath Voltages		-80	V	Voltages Difference for ionization	48	V
	Sample Voltages		-32	V			
E_{Trans}	Buffer Ga	N_2	440	sccm	Voltages Difference for transmission	80	V
	Buffer Voltages		-70	V			
	Pinhole Voltages		-40	V			
Cal	Calibration Flow		10	slpm	Calibration Factor C_{OH} (Reagent ion: $N^{18}O_3^-$)	$1.21*10^{-8}$	cm^3
	Flow Speed		65	cm/s			
	Product It Value		$8.8*10^{10}$	photon/cm^2			
Uncertainties	Sigma		2		Detection Limit ($\times 10^5$ cm^{-3}) (3σ)	In lab	1.7
	Calibration		38%			Day	12
	Overall		44%			Night	8.5

b) CongHua 2022

Efficiency	Parameter	Gas	Values	Units	Specification for Measurement	Values	Units
E_{conv}	Front Injection	SO_2 (0.9%)	5	sccm	Sample Flow [SO_2]	12	ppm
		NO (0.9%)	0.5		Sample Flow [NO]	1.2	ppm
	Pulse Valve	N_2	2	sccm	Cycle Duration (OH)	6	mins
		C_3F_6 (99.9%	2	sccm	Cycle Duration (HO_2)	60	mins
					B/S Ratio (OH)		10%
					B/S Ratio (HO_2)		20%
	Rear Injection	C_3F_6 (99.9%	2	sccm	Sample Flow [C_3F_6]	1072	ppm
		HNO_3	10	sccm	Reaction Time	47	ms
	Sample Flow		3.7	slpm	Sample Flow Speed	55	cm/s
E_{Ion}	Sheath Flow	Zero Air	12.6	slpm	Reynolds Number in Ionization Chamber	>4000 Turbulent flows	
		HNO_3	10	sccm			
		C_3F_6 (99.9%	2	sccm	Sheath Flow [C_3F_6]	159	ppm
	Total Flow		16.8	slpm	Sheath Flow Speed	25	cm/s
	Sheath Voltages		-80	V	Voltages Difference for ionization	48	V
	Sample Voltages		-32	V			
E_{Trans}	Buffer Ga	N_2	440	sccm	Voltages Difference for transmission	80	V
	Buffer Voltages		-70	V			
	Pinhole Voltages		-40	V			
Cal	Calibration Flow		10	slpm	Calibration Factors C_{OH} ($N^{18}O_3^-$) C_{HO2}	$1.09*10^{-8}$	cm^3
	Flow Speed		65	cm/s			
	Product It Value		$8.8*10^{10}$	photon/cm^2		$1.07*10^{-8}$	
Overall Uncertainties (2σ)		OH	44%		Detection Limit in Field Study ($\times 10^5$ cm^{-3}) (3σ)	OH	3
		HO_2*	222%			HO_2*	20

10. *p.8,l.22-23 "Methacrolein (MACR), a derivative of isoprene, is distinctly classified among the biogenically sourced OVOCs for further discussion."*

I could not find any "further discussion".

The sentence mentioning methacrolein (MACR) has been removed from the updated manuscript, as MACR is neither discussed in the main text nor presented in Table 1 in the current version.

Results and Discussion

11. *p.16,l.9. recycling is not a primary source*

We have revised the sentence to clarify that recycling is not a primary source, but a dominant pathway under specific conditions. The updated text reads:

"During midday (10:00–15:00), the recycling of RO species becomes the dominant pathway for HO_2 production, with rates of……"

12. *p.17,l.14-16 "The model calculated average daytime (08:00-16:00) RO2 interference increased HO2 by 127%, 117%, and 144% for PRD, CEC and CNC case, respectively." Reformulate with reference to Text 4S.3 to make it clear that it is about the estimated contribution of RO2 to HO2* signal? Also, see the comment to p.7,l.18 above.*

We have revised the sentence to clarify that it refers to the model-estimated contribution of

RO_2 to the HO_2* signal. The updated sentence now reads:

"According to model simulations (Text S4.3), RO_2 interference was estimated to account for 56%, 54%, and 59% of the observed HO_2* signal for the PRD, CEC and CNC case, respectively."

Revised content on Text S4.3

…, we determine that the average daytime (08:00-16:00) RO_2 interference was estimated to contribute 56%, 54%, and 59% of the HO_2* signal during the PRD, CEC and CNC case, respectively. Throughout the entire campaign, the contribution ranged from 44% to 69%.

13. *p.18,l.9 Figure 8. Replace "PRD" by "CEC"*

Thanks for comment, the figure notion has been corrected by replacing "PRD" with "CEC" as suggested.

14. *p.19,l.9 "substantially higher modeled HO2 concentration than base model" Or than HO2*(obs)?*

Thank you for the suggestion. We have revised the sentence to correctly compare the modeled HO_2 with the observed HO_2* as follows:

"……, while constraining OH still leads substantially higher modeled HO_2 concentration (blue line in Figure 7b) than the observed HO_2^*."

15. *p.19,l.18 "suggesting that there may be missing OH reactivity" It looks more like the result of constraining the model with high HO2 in combination with early morning NO peaks. Hence, either erroneously estimated HO2, or, as suggested, some missing OH loss.*

Thank you for the insightful comment. The reviewer is correct that the early morning OH overestimation could result from either the overestimated HO_2 constraint or from missing OH loss processes. In our model setup, the constrained HO_2 values are already close to the observed HO_2*, representing the potential upper limit of ambient HO_2. Nonetheless, we agree that the possibility of erroneous HO_2 input cannot be excluded. Therefore, we have revised the sentence to reflect both potential explanations.

"However, the OH concentration is overestimated in the morning when the corrected HO_2* was constrained, suggesting that some OH sinks may be missing in the model during this period or the corrected HO_2* values that were used to constrain the model are still higher than the true HO_2 values."