

Thank you for your second-round comments on our manuscript (EGUSPHERE-2022-854). Please find our itemized responses below and the corrections in the re-submitted files. The original comments are in **black**. The responses to the comments are in **blue**. The changes in the manuscript and the supplementary were highlighted in **yellow** and were cited in **purple** in this response.

The revised paper is very much improved, and the authors have responded satisfactorily to my questions and comments. The line of argumentation why unmeasured OH reactants are most likely responsible for the model overestimation of OH is now plausible. I recommend publication of the manuscript after minor revisions.

Response: Thanks for the encouraging comments.

The authors should extend the discussion on missing OH reactivity, as they consider missing OH sinks important enough to mention in the title. The authors estimate the missing reactivity that would be needed to match the modeled OH to the observation. The estimate assumes that the unknown reactant(s) consume OH without subsequent OH recycling. In the lower troposphere, the only relevant OH sink that acts as a radical termination reaction is the reaction of OH with NO₂, which is already included in the model. All other reactions produce either HO₂ or RO₂ which can recycle OH when there is NO present. I suggest that the authors perform sensitivity tests where they include OH recycling when they adjust the missing OH reactivity. They could assume a recycling mechanism for the unknown reactant that behaves, for example, like for CH₄ or CH₃CHO, where the formed RO₂ is partially recycled back to OH with NO. How much additional OH reactivity would be needed in these cases? Can the authors speculate in more detail about the possible origin of the missing reactant(s)?

Response: Thanks for the suggestion on the sensitivity test. We think the suspected missing VOCs should be quite reactive, thus we chose CH₃CHO suggested by the referee for the sensitivity test. Results show that, if the recycling mechanism is considered, on average, additional 19.5 ppb CH₃CHO would be needed as the additional OH sink to match the observation, with a calculated OH reactivity of 7.2 s⁻¹, compared to the calculated k_{miss} in section 3.3.3 (5.0 s⁻¹) without recycling. We have added additional discussion in section 3.3.3 and a revised Figure S4 as shown below:

“We conducted a sensitivity test in which we assume the missing sink is resulting from under-measured CH₃CHO. Results show that CH₃CHO concentrations would increase by 20 times (RUN_{CH₃CHO}) to make up the missing OH sinks and the missing reactivity with cycling of CH₃CHO oxidation product would increase to 7.2 s⁻¹ (Figure S4).”

“

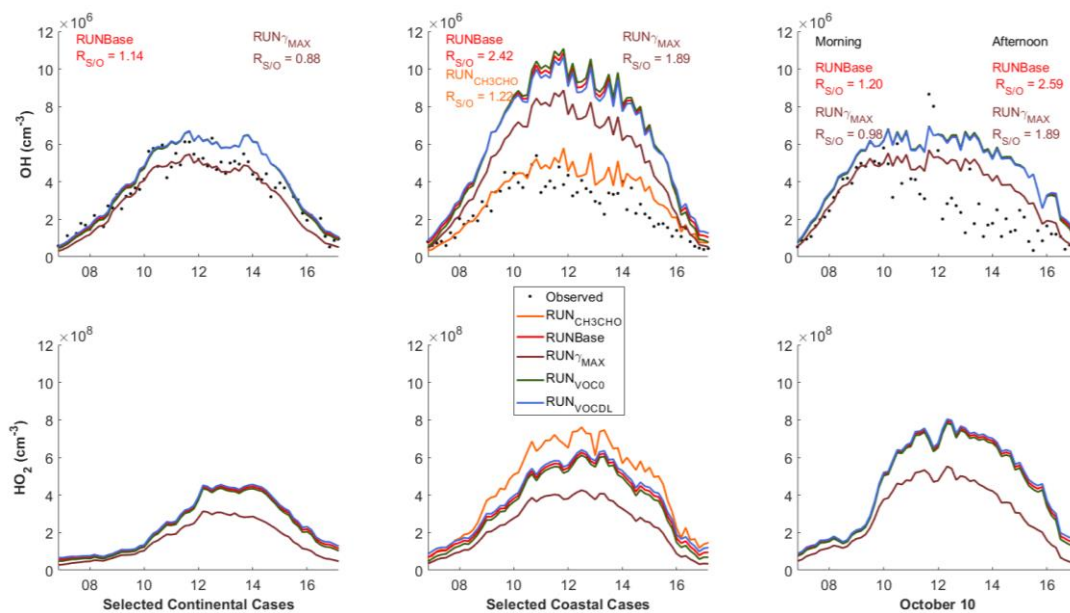


Figure S4. Sensitivity tests for the simulated OH and HO₂ in continental and coastal cases on 10 October. RUN_{CH₃CHO} shows the simulated results of the selected coastal cases when additional CH₃CHO is added as OH sinks. RUN_{γ_{MAX}} shows the simulated results for the maximum heterogeneous uptake effect of HO₂ ($\gamma = 1$). The RUN_{VOC0} and RUN_{VOCDL} show the simulated results that constraints “0” and the detection limit value as the concentration of VOCs when their concentration was below detection limits.”

additional OH reactivity would be needed

Specific comments.

1. Page 1 - Line 25. Missing OH reactivity is generally defined as a pseudo-first order rate coefficient for OH loss by unmeasured reactants.

Response: Thanks for the comments, we agree to the definition and revised the sentence as follows:

“A missing OH reactivity, which is defined as the pseudo-first-order rate coefficient for OH loss by unmeasured trace gases was estimated as $5.0 \pm 2.6 \text{ s}^{-1}$”

2. Page 1 - Line 26 – 28. The sentence is incomprehensible.

Response: Thanks for the comments, we revised the sentence as follows:

“Unaccounted-for OH sinks in the model are proposed to be the cause of this overprediction. A missing OH reactivity, which is defined as the pseudo-first-order rate coefficient for OH loss by unmeasured trace gases was estimated as $5.0 \pm 2.6 \text{ s}^{-1}$ (lower limit) in the coastal air, and the missing reactivity increased with decreasing concentrations of NO_x and volatile organic

compounds (VOCs).”

3. Page 2 - Line 18 – 19. "... tropospheric OH radicals can now be detected...". Sounds strange. These techniques have been measuring atmospheric OH for 30 years.

Response: We deleted “now” in the revised sentence as follows:

“Through decades of efforts, tropospheric OH radicals have been successfully detected following the development of

4. Page 3 – Line 27 – 28. References missing.

Response: The review article (Heard and Pilling, 2003) was added as a reference.

5. Page 4 – Line 2 – 4. The development of the LIM0 mechanism was initially inspired by unexplained high OH concentrations observed during field campaigns in forested regions. Very soon after, laboratory and chamber experiments paved the way for further improvements in isoprene mechanisms that are further developments of LIM0 (for an overview, see Novelli et al., 2020 and Wennberg et al., Chem. Rev. 2018, 118, 3337–3390).

Response: Thanks for the comments. Since the missing sources and the LIM mechanism are not the focus of our article, we reduced the discussion on details of the mechanism and rewrote the relevant content as below:

“The Leuven isoprene mechanism (LIM) was then developed to explain the high OH concentrations observed during field campaigns in forested regions, based on laboratory and chamber experiments of isoprene oxidation (Wennberg et al., 2018; Novelli et al., 2020). With the adoption of this mechanism,

6. Page 7 – Line 6. The sentence should end with ", respectively".

Response: Thanks for the comments, the sentence ended with ", respectively" now.

7. Page 8 – Line 10. "... at 62...". Typo?

Response: Thanks for the careful check, “at 62” is the correct description. However, the label for it should be S₆₂ instead of S₆₄. Based on this comment, the rest of “S₆₄” was changed to S₆₂ in the manuscript and supplementary for consistency.

8. Page 8 – Line 23. "... Table S1...". Table 1?

Response: Thanks for the careful check, it should be Table 1.

9. Page 9, Equation E4. A lower-case symbol (e.g., v) should be used for the mean molecular

velocity. The symbol for molar mass is generally M . Thus, M_{HO_2} would be suitable.

Response: Thanks for the suggestion. The equation has been changed as follows:

$$v_{HO_2} = \sqrt{\frac{8RT}{\pi \times M_{HO_2}}} \quad (E4)$$

10. Page 10 – Line 12 – 13. It is surprising that the correlation with J_{O_1D} is so much worse than with J_{NO_2} . How do these results compare with other observations in coastal regions (for example, Berresheim et al., Atmos. Chem. Phys., 3, 639–649, 2003)?

Response: We appreciate the reviewer's comment. First, the relationships for OH versus J_{O_1D} and OH versus J_{NO_2} are not always linear under different NO_x concentrations (Berresheim et al., 2003; Rohrer and Berresheim, 2006). These relationships become more complicated when O_3 photolysis is not the major HO_x source (Berresheim et al., 2003), as is the case in our study (Table 2). Therefore, we do not compare the linear fit R^2 values for OH versus J_{O_1D} and OH versus J_{NO_2} .

In addition, the relationship between OH and J_{O_1D} has been used to learn about OH production mechanisms when O_3 photolysis is the dominant HO_x source (Berresheim et al., 2003). This is not necessarily applicable in our study when HONO photolysis is 50-70% as strong as O_3 photolysis as a HO_x source (Table 2). Instead, we use the F0AM model with more complete mechanisms to learn about OH production. We show the figures for OH versus J_{O_1D} and OH versus J_{NO_2} (Figure. S2) just to demonstrate that our OH measurements are reasonable. The changes were shown below:

“The OH concentrations showed a distinct diurnal pattern and a positive correlation with J_{NO_2} ($R^2 = 0.68$) and calculated J_{O_1D} ($R^2=0.46$) (Figure S2), similar to the findings in previous studies (Berresheim et al., 2003; Rohrer and Berresheim, 2006; Ma et al., 2019).”

11. Page 10 – Lines 17 – 18. "total measured VOCs reactivity" may be misunderstood as measured reactivity of VOCs. It would be better to say: total reactivity of measured VOCs.

Response: Thanks for the comment, the description for reactivity of VOCs and OVOCs was changed as recommended.

12. Page 11 – Lines 5 – 10. I am surprised about the levels of NO (~ 0.1 ppb) and isoprene (~0.1 ppbv) at night shown in Fig. 4. At the given O_3 mixing ratio of about 40 ppbv and 0.5×10^6 OH/cm³, the expected lifetime of NO and isoprene is 1 min and 4 h, respectively. Is anything known about the sources of NO and isoprene that maintain the observed concentration levels at night?

Response: The nighttime isoprene might be due to the nocturnal emission from the plants surrounding the site. Since the isoprene emission from the plants is closely related to the temperature (Miyama et al., 2013), and most of the nighttime temperature in this campaign was above 20°C (Figure 3), we believe that the nocturnal emission of isoprene from the plant are nonnegligible.

The nighttime NO was due to the emissions from the ships as reported in previous studies (Wang et al., 2019).

The discussion were added as follow:

“Non-negligible levels of NO (~ 0.1 ppb) and isoprene (~ 0.1 ppb) were observed at night, which could be caused by nearby ship emissions and plant emissions, respectively.”

13. Page 13 – Line 2. The symbol p should be defined.

Response: Thanks for the comments, the changes were shown below:

“The coastal air masses showed statistically significant (i.e., p -value < 0.05) lower NO_x (–63%), AVOCs (–47%), BVOCs (–50%), OVOCs (–23%), and CO (–31%) concentrations compared with the continental cases (Figure 7, Table S3). (The p -value is the probability of the difference of two data sets occurs by chance).”

P14. Page 16 – Line 15. "... possible missing source...". Do you mean missing sink?

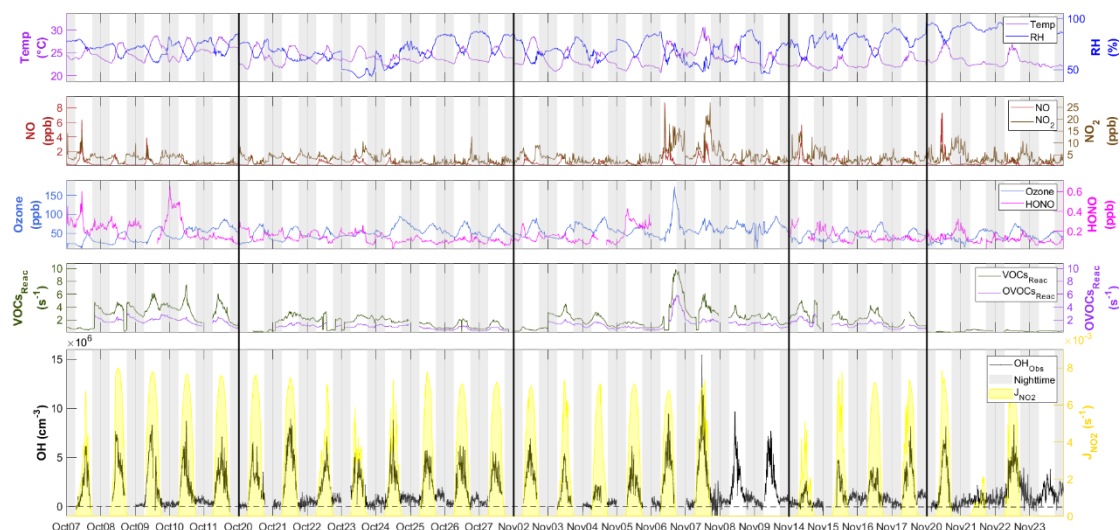
Response: Thanks for the careful check, it should be missing sinks.

15. Page 30, Figure 3. What is the meaning of M in "VOCsReac(M)"? The expression looks like a function on M.

Response: “(M)” denotes “measured”. To avoid confusion, “(M)” was removed from Figures 3,4,7 and 8.

16. Page 30, Figure 3. A horizontal dotted line at OH = 0 would be helpful to understand the diurnal profile of OH.

Response: Thanks for the suggestion, A horizontal dotted line was added, and the revised figure is shown below:



“Figure 3. Time series of OH between 7 October and 23 November with measured weather conditions (temperature and RH), OH primary sources (ozone and HONO), NO_x (NO and NO₂), the reactivity of measured VOCs and OVOCs (VOCs_{Reac} and OVOCs_{Reac}), and photolysis frequency (J_{NO_2}). All measurement data shown are 10 min averages. The gaps in the data were due to calibration or instrument maintenance. The black lines separate the non-continuous days during measurement and the black horizontal dotted line denotes [OH]=0. The grey shaded area denotes night-time. The time zone was the local time (+8 UTC) for the x-axis.”

Supplement in egosphere-2022-854-ATC1.pdf

1. Page 41 – Line 2. Figure 3 must be Figure 2 ?

Response: Thanks for the careful check, it should be Figure 2.

2. Page 41 – Line 12. The quantity "It" is a photon area density (photons/cm²), sometimes called "photon fluence". Please check unit in Table S2.

Response: Thanks for the comment. The unit of “It” in Table S2 was changed to photons/cm². Please see the revised Table S2 in the response for item 10.

3. Page 41 – Eq. SE2. What are the units of TS97, BS96 and S64? In Table S2, the calibration factor C is given in units of OH·cm³/Hz. Please explain!

Response: Thanks for the careful check, the unit of TS97, BS97, and S64 is Hz. However, the Hz were cancelled out in the calculation of the calibration factor (SE2: $C = \frac{1}{[OH]_{CAL}} \times \frac{TS_{97}-BS_{97}}{S_{62}}$). Therefore, the unit of calibration factor (C) should be cm³.

Also, as mentioned above, the “S₆₄” should be “S₆₂” instead. Please see the revised Table S2 in

the response for item 10.

4. Page 41 – Eq. SE3. What about statistical noise of S₆₂? Shouldn't it be included in the calculation of DL?

Response: Thanks for the comment. We should consider the noise of S₆₂ in DL calculation. The corrected equation is shown below:

$$DL = \frac{1}{C} \times n * \sigma\left(\frac{BS_{97}}{S_{62}}\right)$$

Where DL is the detection limit in cm⁻³, C is the calibration factor, and n is the ratio of signal to noise S/N. $\sigma\left(\frac{BS_{97}}{S_{62}}\right)$ represents the standard deviation of the background measurement when the scavenger was added through front injectors. The detection limit (n = 3, average time = 6 minutes) in the laboratory was approximately 1.7×10^5 molecules cm⁻³ on average.”

Based on this equation, the calculated DL will change from 1.5×10^5 to 1.7×10^5 in lab conditions. The DL for daytime and nighttime will change from 10×10^5 to 12×10^5 and 7.7×10^5 to 8.5×10^5 , respectively. Please see the change of detection limits in the revised Table S2 in the response for item 10.

5. Page 41. How large are typical signals (TS₉₇, BS₉₆ and S₆₄)?

The TS₉₇ and BS₉₇ varied from tens to hundreds depending on the ambient chemical conditions, the strength of the reagent ion (S₆₂) signal, and the instrument status. The S₆₂ varied from tens of thousands to 200,000. The S₆₂ could change due to the inlets assembling and change in flows of injection gases and voltages of the CIMS, and the detector aging. That is why we use the ratio between them instead of their absolute signals of TS₉₇ and BS₉₇ for concentration calculation.

6. Page 42 – Line 1. I can't find the information in Figure 8. Wrong/missing Figure?

Response: Thanks for the careful check, Figure 8 is the wrong figure that should not be included in the manuscript. Please see the changes below:

“The detection limit (S/N = 3, average time = 6 minutes) in the laboratory was approximately 1.7×10^5 molecule cm⁻³ on average. ”

7. Page 42 – Line 25. What is the difference between S (sensitivity) and C (Eq. SE2)?

In our study, they both refer to the numerical presentation of the instrument's sensitivity. To avoid confusion, we now use C instead of S in the sensitivity optimization section.

8. Page 43 – Line 23. "C3F8" Typo?

Response: Thanks for the careful check, it should be C₃H₈.

9. Page 43 – Line 23 - 25. I do not understand what the authors mean. Please give a definition of "elimination rate". Why is it larger for C₃F₆ than for C₃H₈? Why does the purity of the gas play a role? What is meant by "stable quality"?

Response: Thanks for the comments. We changed the “elimination rate” to “scavenging efficiency (SE)” which is defined as $SE = \frac{TS97-BS97}{TS97} \times 100\%$. We tested three cylinders of C₃H₈ during optimization, and they gave widely different SE although they are labelled in the same C₃H₈ concentration. We think that the purity of those C₃H₈ cylinder gases was questionable. Stable quality (for C₃F₆) means that compare to C₃H₈, C₃F₆ has a relatively consistent SE (>90%) for all cylinder gases we used regardless of supplier. Please see the changes below:

“We tested both C₃F₆ and C₃H₈ as scavenger gas for OH. We found that the C₃H₈ provided by our suppliers were questionable because the scavenging efficiency ($SE = \frac{TS97-BS97}{TS97} \times 100\%$) by C₃H₈ in the different cylinders and different suppliers varied from 30% to 98% although the cylinders were labelled with the same concentration. In contrast, C₃F₆ from different cylinders labelled with the same concentration gave consistent SE. Therefore, we chose C₃F₆ as the OH scavenger gas.”

10. Page 45, Table S2. Check the given detection limits (missing units!).

Response: Thanks for the careful check, the unit ($\times 10^5 \text{ cm}^{-3}$) was added to the detection limits in Table S2. The revised table S2 is shown below:

Efficiency Related	Parameters	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 ₃ F ₆ (99.9%)	2	sccm	Scavenging Efficiency (OH)	92%	
	Rear Injection	C ₃ F ₆ (99.9%)	2	sccm	Sample Flow [C ₃ F 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 ₃ F ₆ (99.9%)	2	sccm	Sheath Flow [C ₃ F 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 Gas	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 (Reagent ion: NO ₃ ⁻)	1.21*10 ⁻⁸	cm ³
	Flow Speed		65	cm/s			
	Product It Value		8.8*10 ¹⁰	photon/cm ²			
Uncertainties		Sigma (σ)	2		Detection Limit (10 ⁵ × cm ⁻³)	In the lab (3 σ)	1.7
		Calibration	38%			Daytime (3 σ)	12
		Overall	44%			Nighttime (3 σ)	8.5

11. Page 47, Table S3. For which time of day do the average values apply?

Response: The concentrations in Table S3 were averaged the daytime (6:00 to 18:00). The following sentence was added to the notes of the table:

“The concentration was averaged from the daytime (6:00 to 18:00) results.”

Reference:

Berresheim, H., Plass-Dülmer, C., Elste, T., Mihalopoulos, N., and Rohrer, F.: OH in the coastal boundary layer of Crete during MINOS: Measurements and relationship with ozone photolysis,

Atmospheric Chemistry and Physics, 3, 639–649, <https://doi.org/10.5194/acp-3-639-2003>, 2003.

Heard, D. E. and Pilling, M. J.: Measurement of OH and HO₂ in the Troposphere, *Chem. Rev.*, 103, 5163–5198, <https://doi.org/10.1021/cr020522s>, 2003.

Ma, X., Tan, Z., Lu, K., Yang, X., Liu, Y., Li, S., Li, X., Chen, S., Novelli, A., Cho, C., Zeng, L., Wahner, A., and Zhang, Y.: Winter photochemistry in Beijing: Observation and model simulation of OH and HO₂ radicals at an urban site, *Science of The Total Environment*, 685, 85–95, <https://doi.org/10.1016/j.scitotenv.2019.05.329>, 2019.

Miyama, T., Okumura, M., Kominami, Y., Yoshimura, K., Ataka, M., and Tani, A.: Nocturnal isoprene emission from mature trees and diurnal acceleration of isoprene oxidation rates near *Quercus serrata* Thunb. leaves, *Journal of Forest Research*, 18, 4–12, <https://doi.org/10.1007/s10310-012-0350-5>, 2013.

Novelli, A., Vereecken, L., Bohn, B., Dorn, H.-P., Gkatzelis, G. I., Hofzumahaus, A., Holland, F., Reimer, D., Rohrer, F., Rosanka, S., Taraborrelli, D., Tillmann, R., Wegener, R., Yu, Z., Kiendler-Scharr, A., Wahner, A., and Fuchs, H.: Importance of isomerization reactions for OH radical regeneration from the photo-oxidation of isoprene investigated in the atmospheric simulation chamber SAPHIR, *Atmos. Chem. Phys.*, 20, 3333–3355, <https://doi.org/10.5194/acp-20-3333-2020>, 2020.

Wang, T., Dai, J., Lam, K. S., Nan Poon, C., and Brasseur, G. P.: Twenty-Five Years of Lower Tropospheric Ozone Observations in Tropical East Asia: The Influence of Emissions and Weather Patterns, *Geophysical Research Letters*, 46, 11463–11470, <https://doi.org/10.1029/2019GL084459>, 2019.

Wennberg, P. O., Bates, K. H., Crounse, J. D., Dodson, L. G., McVay, R. C., Mertens, L. A., Nguyen, T. B., Praske, E., Schwantes, R. H., Smarte, M. D., St Clair, J. M., Teng, A. P., Zhang, X., and Seinfeld, J. H.: Gas-Phase Reactions of Isoprene and Its Major Oxidation Products, *Chem. Rev.*, 118, 3337–3390, <https://doi.org/10.1021/acs.chemrev.7b00439>, 2018.