

Response to reviewers for the paper “A comprehensive evaluation of enhanced temperature influence on gas and aerosol chemistry in the lamp-enclosed oxidation flow reactor (OFR) system” in Atmos. Meas. Tech. Discuss. Doi: 10.5194/amt-2023-230

By Tianle Pan et al.

We appreciate the three reviewers' comments and support for the publication of this manuscript after revisions. Following the reviewers' suggestions, we have carefully revised the manuscript. To facilitate the review process, we have copied the reviewer's comments in black text. Our responses are in regular blue font. We have responded to all the referee comments and made alterations to our paper (**in bold text**).

Anonymous Referee #3

The authors have significantly improved the language and satisfactorily responded to some of my comments. However, I cannot find this revision acceptable because the authors did not respond to all of my remarks. I submitted 4 pages of comments, but the authors only responded to the comments in the 2 first pages.

We are sincerely sorry that we forgot the last two pages in the last round of revision. Here we attached the rest responses from last round. The sequence number for each comment was continued with the first two pages and start with question “R3.18”. The responses for the new comments are also addressed point by point in the following.

R3.18: p. 12 l. 352: Here and elsewhere the authors use term ‘OFR tubes’ for the OFR casing. I would suggest finding a better term, since to my understanding this structure consists of a single large tube and the end plates, not ‘tubes’.

A3.18: We replaced all the “OFR tubes” with “**OFR enclosure**”.

R3.19: p. 13 l. 395: was → is

A3.19: Corrected.

R3.20: p. 13 l. 396: What is ‘more even and better-mixed air’? I think the purpose of the ring flow manifold is to reduce dead space at the end of the OFR and thus reduce the mixing.

A3.20: Yes, the ring flow manifold can reduce the dead space within the OFR. In our text, “more even and better-mixed air” means the airflow within OFR is more uniform as there is less recirculation, which also leads to a better mixing for the gas within OFR, such as the mixing between the precursors and oxidant. In order to reduce ambiguity, we have made modifications in the text:

“In addition to aerosol sampling, the air for gas phase measurements is usually sampled through a perforated ring flow manifold in the back of the PAM-OFR to reduce wall effects and recirculation, which makes the airflow more stable and uniform (Fig. S1).”

R3.21: p. 13 l. 397: Please check the tense of this sentence. Also, the flow distribution certainly will be different, so the word ‘might’ is not necessary here.

A3.21: Corrected.

R3.22: p. 13 l. 409-411: The definition of “sum of integrals of signal over time versus the sum of signals” is not correct. Please define the mean residence time correctly or just cite the relevant source.

A3.22: We deleted the description of the average residence time calculation.

“Details of the τ_{avg} calculation can be found in Huang et al. (2017).”

R3.23: p. 13 l. 412: Here and elsewhere: the authors have measured RTDs and thus also the mean residence times. “Average RTD values” is not correct term.

A3.23: We replaced the “Average RTD values” with “**average residence time (τ_{avg})**”.

R3.24: p. 14 l. 427: calculation → simulation?

A3.24: Changed to “**simulation**”.

R3.25(a): p. 14 Fig. 7: In panels a, c and e, there are 4 different cases in each panel. I

assume these represent the situation at probing depths of 100, 200, 300 and 400 mm. Please indicate this somehow in the figure or in the caption.

A3.25(a): Thanks for the suggestion, we added the statement in both the figure and caption.

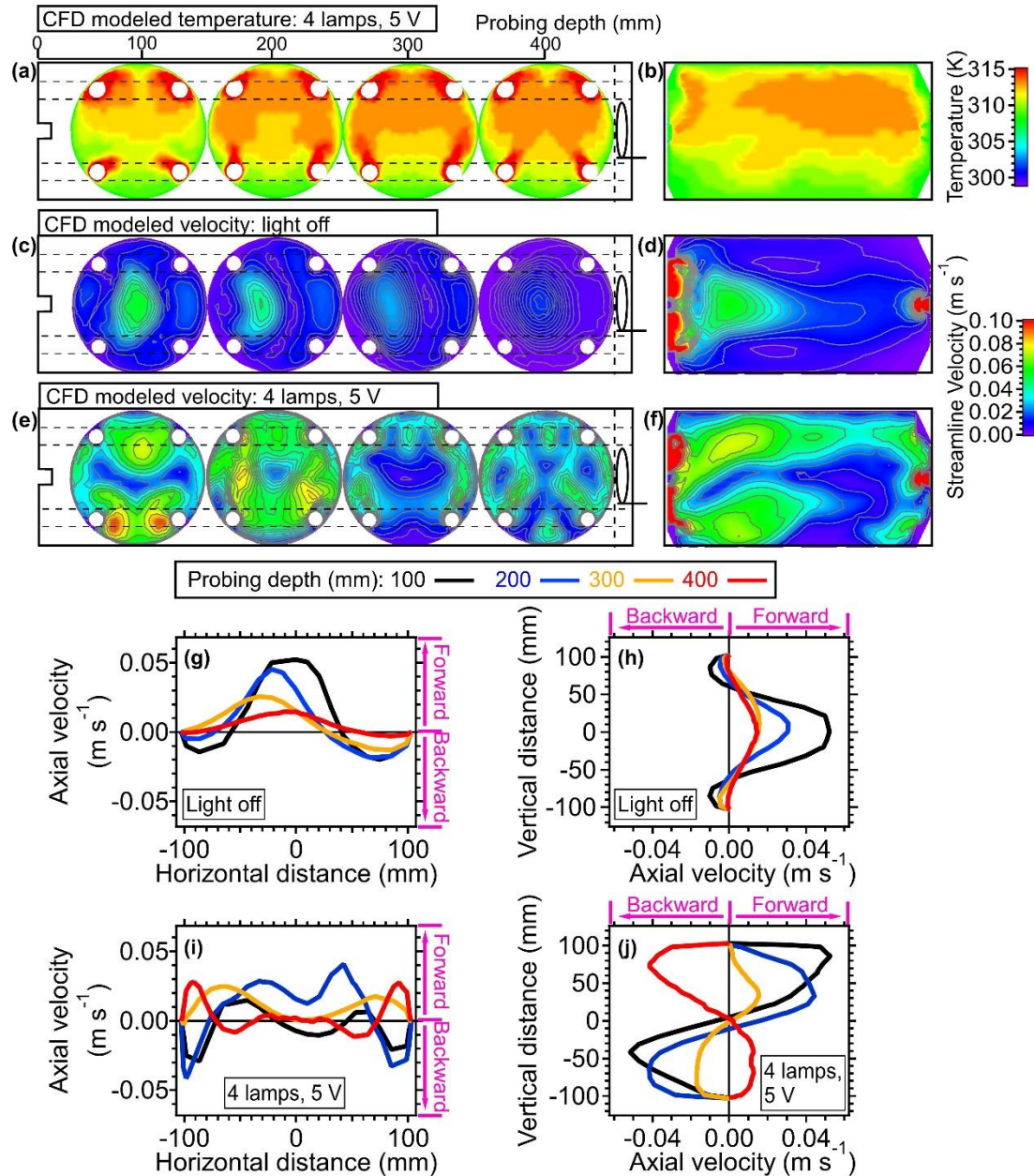


Figure 7: (a) Three-dimensional simulation results demonstrating the cross-sectional temperature profiles. Four cross-sectional figures from left to right represented the results at probing depths of 100, 200, 300, and 400 mm for panel (a), (c), and (e). (b) Simulated lateral temperature profile inside of the OFR based on CFD simulation. Panel (a) and (b) were simulated with conditions that four

lamps were set to be 5 V. (c) Three-dimensional simulation results illustrating cross-sectional velocity profiles and (d) lateral velocity profiles based on CFD simulation results. Panel (c) and (d) were simulated with conditions that lamps were off (room temperature: 25 °C). (e-f) the same plots as panels (c-d) with four lamps set to 5 V. One-dimensional axial velocity profiles at (g) horizontal and (h) vertical directions inside the OFR at room temperature, and one-dimensional axial velocity profiles at (i) horizontal and (j) vertical directions with four lamps set to 5 V. The positive values indicated the velocity direction from inlet to outlet (Forward) and the negative values represented the velocity direction from outlet to inlet (Backward).

R3.25(b): In panels g-j: What does the horizontal or vertical velocity mean? If these are the velocities towards the horizontal or vertical direction, then the labels ‘backward’ and ‘forward’ do not make sense. Or should it be axial velocity?

A3.25(b): They are the axial velocity at horizontal or vertical directions. The positive values of velocity indicate the velocity direction from inlet to outlet (‘Forward’ in the graph). We added the explanation in the caption as shown in A3.25(a).

R3.25(c): Figure caption: “Enhanced temperature influences in panels (c) and (d) were considered” – should this be panels (e) and (f)? The last reference to panel (h) should be (j).

A3.25(c): Yes, we meant that panels (e) and (f) were the results with enhanced temperature influences based on panels (c) and (d). We deleted this sentence for clarity. We also revised the caption for the panel (j). Results could be seen in A3.25(a).

R3.26: p. 15 Fig. 8: The y axis label should be “Probability density function” (or Residence time distribution) with unit of s^{-1} , not “probability distribution function”. In figure caption, “The average RTD values were also estimated here” → “The mean (average) residence times are also shown here”. The calculation of the mean residence time is not an estimate, but a well-defined property of the RTD.

A3.26: We revised the y axis label to “**Probability density function (s⁻¹)**” and modified the caption as “**The average residence times are also shown here**”.

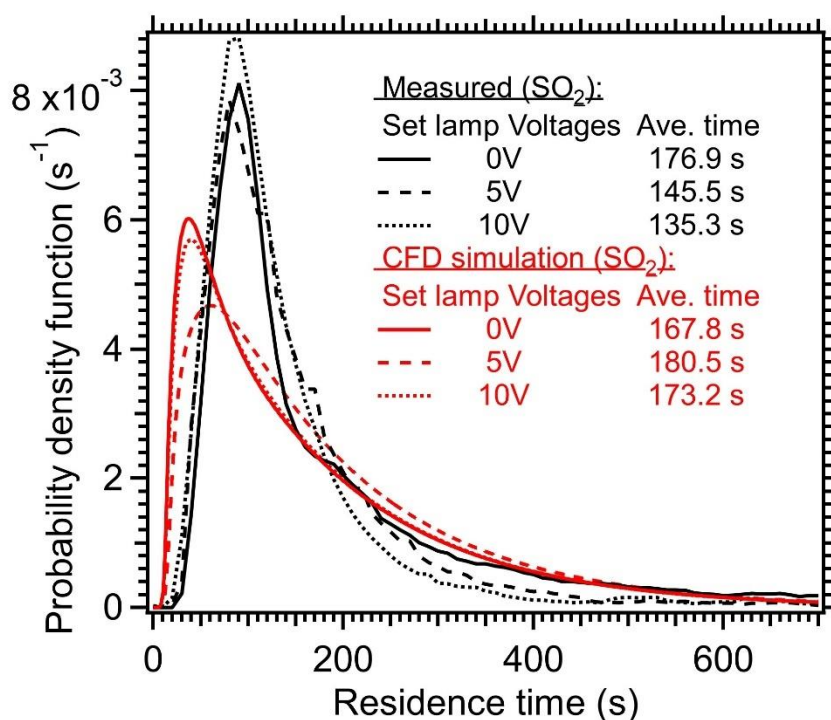


Figure 8: Residence time distribution (RTD) of SO₂ within the PAM-OFR under different lamp settings. A 2 s pulser of SO₂ was injected into the OFR. The average residence times are also shown here. The simulated results from CFD model are shown in red lines.

R3.27: p. 15 l. 456: RTD distributions → RTDs

A3.27: Corrected.

R3.28: p. 15 l. 460: reaction rates, concentrations of

A3.28: Corrected.

R3.29: p. 16 l. 467: “very minor to negligible impact on the gas-phase reactions”. This is too strong a statement since only a limited set of gases and their reaction pathways was studied.

A3.29: We modified the sentence: “**Our results suggested that an increase in temperature within OFR due to lamp heating would have a minimal impact on gas-phase reactions**”.

R3.30: p. 16 l. 485: per (°C second) → s⁻¹°C⁻¹

A3.30: Corrected.

R3.31: p. 16 l. 487: mass loss of ~32% for ambient OA

A3.31: We revised the sentence.

R3.32: p. 17 l. 492: “might” is unnecessary here

A3.32: Corrected.

R3.33: p. 17 l. 519-520: unclear sentence

A3.33: We modified the sentence:

“Note that in the model we did not specifically treat the temperature effect on autoxidation reaction rate of RO₂. E.g., varied yields of highly oxygenated organic molecules (HOMs) from autoxidation shall be used at different temperatures, while constant yields for HOMs were used during the simulation in this study.”

R3.34: p. 17 l. 521: “Using a constant yield for HOMs...” → “The constant yield for HOMs used in this model might...”

A3.34: We revised the sentence according to the reviewer’s suggestion.

R3.35: p. 18 l. 534: “As the detailed...” → “The detailed...”

A3.35: Corrected.

R3.36: p. 19 l. 557-558: Unclear sentence. Consider e.g. “Increasing H_{vap} increases the sensitivity of SOA formation to temperature”.

A3.36: We revised the sentence according to the reviewer’s suggestion.

R3.37: p. 19 l. 561: what does “based on different species and temperature” mean?

A3.37: We revised the sentence: **“These variations were observed across different precursors and temperatures.”**

R3.38: p. 19 Fig. 11: Is the 30 µg/m³ the inlet concentration? And is the x-axis in panels

b and d the inlet concentration of OA?

A3.38: Yes, both concentrations are the inlet concentration. We modified the captions of Fig.11 and other graphs to point out the OA mass concentration is inlet concentration.

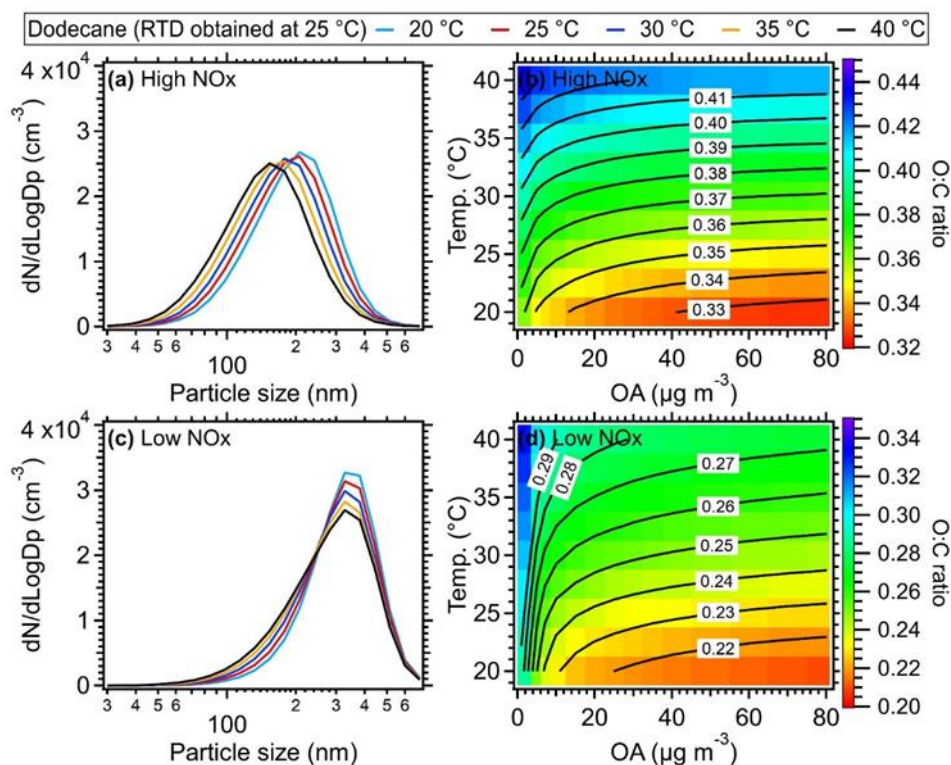


Figure 11: Size distribution of dodecane SOA at different temperatures under (a) high NOx and (c) low NOx conditions, respectively. A mass concentration of $30 \mu\text{g m}^{-3}$ for OA seed (inlet mass concentration) was assumed for size distribution simulation here. The O:C ratio of dodecane SOA as a function of temperature and mass concentration of OA seed (inlet mass concentration) under (b) high and (d) low NOx conditions. The equivalent aging time was 1 day by assuming the ambient OH concentration equated to $1.5 \times 10^6 \text{ molecule cm}^{-3}$ (Mao et al., 2009).

R3.39: p. 19 Fig. 12: “the ambient OH concentration”

A3.39: Corrected.

R3.40: p. 20 l. 572-573: “which shows varied extents for different precursors and reaction conditions” – what does this mean?

A3.40: We modified this sentence as:

“In summary, the heating effect induced by the lamps could significantly influence the SOA formation within OFR for certain high-OH exposure applications. This impact of temperature varied depending on the specific precursors and reaction conditions.”

R3.41: p. 20 l. 573: deceased → decreased

A3.41: Corrected.

R3.42: p. 20 l. 583: reducing → reduce

A3.42: Corrected.

R3.43: p. 20 l. 590: deduction → reduction

A3.43: Corrected.

R3.44: p. 20 Fig. 13: bellowing → blowing

A3.44: Corrected.

R3.45: p. 22 l. 621: trends → hystereses?

A3.45: We replaced “trends” with “**concentration curves**”.

R3.46: p. 22 l. 639-640: is the shorter residence time really due to accelerated diffusion?

A3.46: The temperature gradients in the OFR caused by the UV lamps lead to the axial dispersion (the strengthening effect of molecular diffusion) and thus influence the residence time (Lambe et al., 2019). We revised the text:

“The pulsed tracer measurements suggested that the increased temperature in the PAM-OFR induced the axial dispersion (Lambe et al., 2019), leading to a shorter average residence time (τ_{avg})”

Anonymous Referee #3 (New comments for the second rounds)

R3.47: In addition, regarding my earlier comment (R3.6) and the authors' response (A3.6), there are still conflicting statements in the manuscript. In their response, the

authors say that the SOA formation was simulated under different temperatures directly, but the text in the manuscript does not support this. Some examples are listed below.

A3.47: Thank you for your comments. We revised point-by-point based on reviewer's suggestion.

R3.47(a): -The authors say in their response that no OA seed was considered. However, in p. 7, l. 221 and p. 18, l. 519 they write that the SOA formation was modeled under different OA concentrations (1-80 $\mu\text{g}/\text{m}^3$).

A3.47(a): Sorry for the mistake in R3.6, we meant that we did not consider the evaporation and reaction for the OA seed in simulation. We have revised the description in the main text:

Line 220-222: **"In this study, SOA formation from four typical VOC precursors including dodecane, α -pinene, toluene, and m-xylene was modeled under different OA seed concentrations (1-80 $\mu\text{g m}^{-3}$) and NO_x conditions (low NO_x vs high NO_x). We did not consider the evaporation and reaction of OA seed in the model."**

Line 520-521: **"The evaporation and chemical reaction of existing OA seed under different temperatures were not considered in the model."**

R3.47(b): -p. 18, l. 516: "For the newly formed SOA in the OFR, the temperature impact was simulated..." So here SOA is first formed (independent of temperature), and then the temperature effects on that SOA are studied? I think the temperature effect on the SOA formation itself should be studied.

A3.47(b): Actually, we simulate the SOA formation under different temperatures directly. We revised the sentence:

Line 517-518: **"The formation of SOA from the oxidation of different VOC precursors within OFR was simulated at different temperatures using the SOM model".**

R3.47(c): -p. 18, l. 524: "the higher temperatures result in lower SOA yields due to the increased evaporation of gas-phase products." I disagree. I think at higher temperatures

some of the oxidation products never condense onto particle phase, which leads to a lower SOA yield. So some compounds just stay in the gas-phase, which does not mean evaporation. Again, here it seems like a constant SOA mass is formed independent of temperature, and then the evaporation is modeled at different temperatures.

A3.47(c): We agree with the reviewer. The sentence needs to be clarified. We modified the sentence:

Line 526-527: **“the higher temperatures result in lower SOA yields due to the increased partitioning of oxidation products in gas-phase”.**

R3.47(d): -p. 20, l. 576: Here the authors address the evaporation as well.

A3.47(d): We revised the sentence:

Line 579-581: **“The higher O:C at higher temperatures was probably caused by the less partitioning of semi-volatile and less-oxidized components into particle phase with increased temperatures”.**

R3.47(e): -p. 20, l. 579: Also here the authors talk about evaporated SOA mass.

A3.47(e): We revised the sentence:

Line 582-583: **“In the model, the gas-particle partitioning of oxidation products as a function of temperature was mainly determined by the enthalpy”.**

R3.48: -p. 18, l. 514: "Obvious SOA decrease mass was observed in OFR at different temperatures." Please rephrase this, or in my opinion this sentence is not needed here, since the authors later report the results of the laboratory experiments (p. 18, l. 529).

A3.48: We deleted the sentence as the reviewer's suggestion.

Reference

Huang, Y., Coggon, M. M., Zhao, R., Lignell, H., Bauer, M. U., Flagan, R. C., and Seinfeld, J. H.: The Caltech Photooxidation Flow Tube reactor: design, fluid dynamics and characterization, Atmospheric Measurement Techniques, 10, 839-867, <https://doi.org/10.5194/amt-10-839-2017>, 2017.

- Lambe, A. T., Krechmer, J. E., Peng, Z., Casar, J. R., Carrasquillo, A. J., Raff, J. D., Jimenez, J. L., and Worsnop, D. R.: HO_x and NO_x production in oxidation flow reactors via photolysis of isopropyl nitrite, isopropyl nitrite-d₇, and 1,3-propyl dinitrite at $\lambda = 254, 350, \text{ and } 369\text{nm}$, *Atmospheric Measurement Techniques*, 12, 299-311, <https://doi.org/10.5194/amt-12-299-2019>, 2019.
- Mao, J., Ren, X., Brune, W. H., Olson, J. R., Crawford, J. H., Fried, A., Huey, L. G., Cohen, R. C., Heikes, B., Singh, H. B., Blake, D. R., Sachse, G. W., Diskin, G. S., Hall, S. R., and Shetter, R. E.: Airborne measurement of OH reactivity during INTEX-B, *Atmospheric Chemistry and Physics*, 9, 163-173, <https://doi.org/10.5194/acp-9-163-2009>, 2009.