The authors thank the reviewer for the careful review of our manuscript and the helpful comments and suggestions. All the comments (in black) are addressed point by point, with our response in blue, and the corresponding revisions to the manuscript in red.

Review # 2

Gao et al. presented a newly designed Wall-Free Particle Evaporator (WALL-E) inlet for online chemical measurements of atmospheric particles using a chemical ionization mass spectrometer (CIMS). The authors claim WALL-E can efficiently evaporate organic particles with minimum thermal decomposition, which can be a good technique for real-time particle characterization. However, some sections are not very clear or convincing, which makes me unsure about the reliability of WALL-E. Please see my comments below for more details. Thus, I suggest major revision before publishing this paper.

General comments:

1. I have several questions about the thermal profile of WALL-E system:

1). The temperature profile in Figure 2 is based on the COMSOL simulation. Although COMSOL is a powerful tool to understand the system's thermodynamics, which is good for system design, the simulation results might not match the real results. Please comment on this by discussing the difference between the simulation results and real conditions. I suggest adding some temperature measurements to confirm the temperature profile. You can add a thermocouple at the center of the tubes. This is also important for your temperature correction.

We conducted temperature measurements using a thermocouple placed at the center of the tube to validate the COMSOL simulation. As shown in the updated Figure S13, the measured and simulated temperature profiles are in good agreement. To account for any remaining differences, we used the mean of the two profiles as a correction function for temperature calibration.

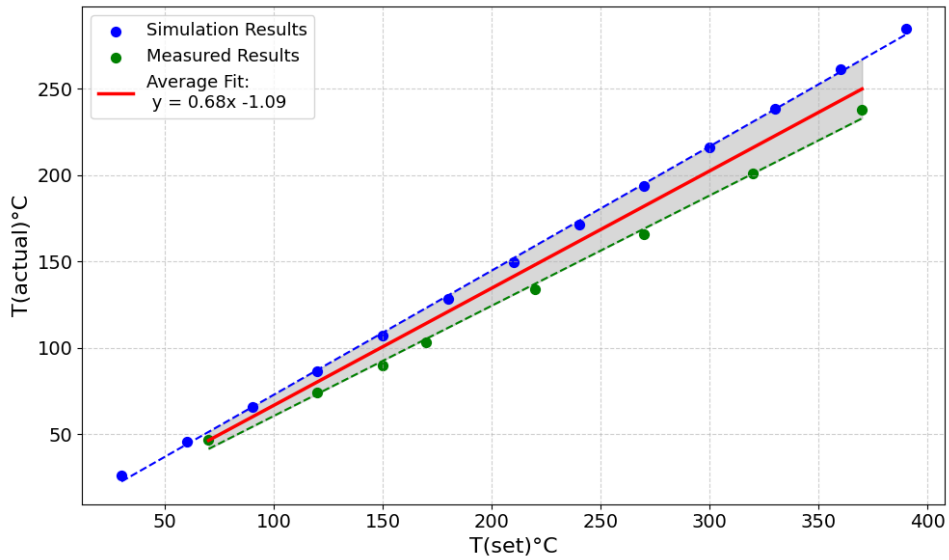

Figure S13. WALL-E temperature correction. T_{set} represents the set temperature for both hot sheath flow and TD and T_{sim} and T_{meas} represent the simulated and measured temperatures.

2). Are there any reasons that you don't put any insulation outside the WALL-E system to prevent the thermal exchange with the ambient?

We confirm that insulation is installed around every heated part of the system to minimize heat exchange with the ambient environment and ensure stable thermal conditions during operation. This is not represented in Figure 1 to ease the visualization of the interface.

Lines 164 – 165: *"All heated regions are insulated to minimize heat exchange with the ambient environment."*

3). In the Dilution/cooling unit, I do not understand how this can prevent the re-condensation of vaporized species. I expect less volatile species could condense on the wall. I think you need to do more tests with different ambient relevant species to investigate this.

The cooling and dilution units are specifically designed to minimize re-condensation by introducing a sufficient flow of nitrogen and ensuring fast transfer to the mass spectrometer. Based on the WALL-E configuration, the residence time in the cooling section is very short, estimated between 0.1 and 0.15 seconds, which effectively prevents re-condensation under the tested conditions. We would like to point out that a similar approach is used on the VIA-NO_3 interface (Zhao et al., 2024). While we cannot certify the lack of nucleation/recondensation within WALL-E, this has not been observed in the VIA-NO_3 interface, while the smaller dilution ratio (3:7) and the longer residence time in the cooling part are more favorable to observe the recondensation of highly oxidized species within the VIA interface.

4). Also, the thermal decomposition was only checked for one species. I suggest adding more standards to validate that, especially those relevant to ambient organics.

In this study, citric acid was selected as a representative compound to assess thermal decomposition because it is a widely recognized benchmark used in previous studies (e.g., Yang et al. (2021)). Its well-characterized and rich decomposition behavior makes it particularly suitable for evaluating the thermal stability of organic compounds in thermal desorption systems, as shown in previous studies (e.g., FIGAERO). As a result, citric acid was used to compare the performance of WALL-E with other systems. Investigating the potential thermal decomposition of a variety of compounds would be the scope of a dedicated study that has been performed by Yang et al. (2021). and is outside the scope of this work.

2. I also have a hard time following the SOA sections.

1). Why do you add SO2 in the SOA generation? It seems very unusual in the literature. You will generate organic sulfate, which can lead to more complicated properties. This also lead to challenges to compare with any literature values (e.g., chemical composition, volatility, thermal properties, etc.)

We added SO_2 to promote particle formation (Stangl et al., 2019) by forming sulfuric acid (H_2SO_4) via the reaction between SO_2, OH, and O_3, but not to investigate S-containing organic species. Indeed, the mass fractions of S-containing organic species are very low (<5%) in all cases (SOA mass between 1 – 15.6 µg m^{-3}). Adding SO_2 prevents the use of very high VOC and O_3 concentrations due to the small residence time within the aerosol flow reactor to produce SOA. Therefore, the change of properties (e.g., chemical composition, volatility) of the SOA is expected to be limited in this study.

We modified the sentence in Line 251: *"SO_2 is injected from a commercial cylinder (500 ppm, AIR PRODUCTS Inc.), to promote the particle formation and to generate more SOA mass."*

2). I do not understand how you did sensitivity corrections. Please explain that a little bit more.

The key step of sensitivity correction is to determine the correlation between sensitivity and dV_{50} (voltage difference at half signal maximum intensity) as proposed in Figure S8. This is obtained by using the standard compounds exhibiting different binding energy (i.e., sensitivity). Then, according to the function derived from Figure S8, the concentration of the different particle phase species can be estimated after measuring their dV_{50} values from the CID scanning as described by Lopez-Hilfiker et al. (2016). We clarify the sensitivity correction in the following section

Lines 385 – 388: *"The correlation between sensitivity (Figure S2) and dV_{50} (Figure S7) is obtained based on the standard compound, as depicted in Figure S8. By applying this sigmoidal function and using the dV_{50} values determined for individual α-pinene-derived SOA products, the concentration of every oxidation compound can be estimated."*

3). It is very surprised to me that your SOA mass derived from CIMS is much higher than that from SMPS. Those results do not convince me since I expect the mass to be underestimated by CIMS due to evaporation and transport efficiency, re-condensation on the wall, and loss of volatile species in the activated carbon denuder in WALL-E. I do not really understand why WALL-E leads to overestimation.

The uncertainties pointed out by the reviewer are already included within the calibration factors derived from the introduction of the different standards (i.e., Figures S2 and S7-8). The overestimation is not related to the WALL-E interface but to the uncertainties related to the declustering method as discussed in previous work (e.g., Lopez-Hilfiker et al., 2016). For example, the presence of different isomers can lead to very different calibration factors (Lee et al., 2014). We would like to point out that the quantification obtained for sulfuric acid is within very good agreement (i.e., 7% using 8-compound fitting) between the direct calibration (i.e., Figure S2 and the concentration retrieved by the declustering scan method. While suffering from some uncertainties, the declustering scan represents a unique opportunity to provide a semi-quantification of all compounds present in the particle phase for untargeted analysis. We respectfully disagree with Reviewer #2 that the SOA mass derived from the chemical characterization is "much higher" than from SMPS. Uncertainties related to CIMS quantification have often been reported to be 50-100%. A dedicated work will be required to narrow down the uncertainties by notably using non-commercial standards (e.g., Gagan et al., 2023; Kenseth et al., 2023), which is outside the scope of this study.

3. I do not find discussion about volatility based on their measurements.

In this work, we focus on characterizing the system performance and introducing the capability to estimate volatility. A more detailed and comprehensive volatility analysis, particularly for relevant SOA systems, will be addressed in future studies.

4. Are there any size dependencies in your results?

This has been previously discussed in Zhao et al. (2024), who showed that the evaporation within the TD is not size-dependent at temperatures greater than 300°C. All experiments

performed in this work (besides the temperature ramp) were performed at 320°C, so we do not expect any size dependencies in the results presented here.

5. What is the sensitivity and detection limitation of using WALL-E?

The corresponding sensitivity of α-pinene-derived SOA compounds generally increases with molecular mass and reaches a plateau corresponding to the maximum sensitivity (i.e., collision limit), as shown in Figure S10. This indicates an upper limit of sensitivity of 0.08 ncps·per·μg·m^{-3}, yielding a detection limit of about ~5-10 pg·m^{-3} (assuming a detection limit with the CIMS of $5 \times 10^{-6} - 1 \times 10^{-5}$ as discussed in Riva et al. (2020)).

We revised lines 393 - 395: *"with an upper limit of sensitivity of 0.08 ncps·per·μg·m^{-3} providing a limit of quantification ~5-10 pg·m^{-3} corresponding to uncorrected signal intensities of $5 \times 10^{-6} - 1 \times 10^{-5}$ (Riva et al., 2020)."*

Specific comments:

1. could you label each part and the flow direction? I also do not understand why there are two tees for the sheath flow. Is WALL-E like a distillation tube where a sample tube is inserted inside a big tube? Then why are these tees in the same position?

As mentioned in comment #4 of reviewer #1, Figure 1 has been revised to provide a clearer visual understanding of the setup

2. Section 2.2.1. It is unclear to me how you mixed these solutions. What is the fraction of each chemical?

We mixed these standard chemicals in water, with the concentration of each to be 1 ppm. To clarify, we add a sentence:

Lines 222 – 223: *"The concentration of each chemical in the aqueous solution is 1 ppm."*

3. L330-331, "Without sensitivity … ug m-3." The signal is only 0.04 ncps, which is the same as the signal that no VOC was injected (L326). Therefore, the SOA signal could just be the background noise.

The mass spectra presented in this work (including Figure 4 and lines 330-331) are background-subtracted. The total signal of all detected SOA compounds is ~0.08 ncps (without background subtraction) and ~0.04 ncps (after background subtraction) when the particle mass is 1.0 ± 0.1 μg m^{-3}. However, the high background of 0.04 ncps in line 326 refers to the individual compound $C_8H_{12}O_4$, which could be a contamination compound from the flow tube. Therefore, the SOA signal must not be the background noise.

4. Figure S6. I suggest using scattering plots with fittings.

Figure S6 is now in scattering plots with fittings.

5. Figure numbers in SI need to be correct.

They are now corrected.

6. dV50 is not well defined.

The definition is now added.

7. L387-389, "Using the dV50 … 8-compound fitting)." Do you expect that high amount of H2SO4? How much SO2 was added to the system?

Yes, we expect a high amount of H_2SO_4 of 6.4 – 8.7 µg m^{-3} in the case of SOA mass of 15.6 µg m^{-3}. SO_2 concentration is 31 ppb as reported in Table S3.

8. Section 3.3.2. I think either T_{max} or T_{50} works for discussing the volatility, but you are mixing them up and making it hard for me to follow. I suggest either picking one or separating them into two sections.

In this work, we discuss both T_{max} and T_{50} to provide continuity with previous studies while also introducing the benefits of using T_{50}. To improve clarity, we have revised this section to separate the discussion of each parameter better and indicate when T_{max} is used for comparison purposes and when T_{50} is applied for volatility estimation.

Line 447: *"3.3.2 T_{50} as a Robust Volatility Metric"*

Lines 490-493: *"Although T_{50} is introduced as a more robust metric in this study, temperature correction and inter-comparison with other techniques have traditionally been performed using T_{max} values. Therefore, we present the correction and comparison based on T_{max} to ensure consistency with previous studies before applying the T_{50} approach."*

Lines 517 – 520: *"3.3.4 Volatility Estimation from T_{50}*

As previously explained, the use of T_{50} would provide a more reliable estimation of the volatility, in the case of WALL-E, which is typically inferred using the relationship between T_{50} and the saturation concentration (C^*) as discussed in prior studies (Ylisirniö et al., 2021)."

9. L454-455, "For comparison … of 98%." Why do you use 98%, not 99.5% or 99.9%, as other studies you mentioned before?

In prior studies, T_{max} was straightforward to determine due to Gaussian-shaped thermograms. In our case, the WALL-E thermograms follow a more sigmoidal shape, making T_{max} less robust and highly sensitive to the selected threshold. To demonstrate this, we conducted a sensitivity analysis (Figure S12), which shows that while the absolute T_{max} values vary slightly with the threshold (e.g., 98% vs. 99.9%), the trend and slope of the volatility comparison remain unchanged. We selected 98% because it better aligns with the observed signal maxima, offering more representative T_{max} values for comparison purposes.

Lines 470-473: *"In contrast to earlier systems, including the FIGAERO and VIA, which often produce Gaussian-shaped thermograms with clearly defined peaks, WALL-E thermograms follow a sigmoidal profile. This makes the determination of T_{max} more sensitive to the selected threshold and prone to variability, especially at upper temperature ranges."*

10. L457-458, "In addition … fewer data points." Do you mean fewer data points at higher temperatures? Overall, you have lots of data points, and it seems that only PEG-17 do not have enough data points after reaching the T_{max}.

This limitation mainly affects PEG-17, while sufficient data points are available for the other PEGs.

Lines 479-481: *"In addition, at higher temperatures, the fit for less volatile PEGs can result in more errors due to fewer data points, which mainly affect PEG-17. Taking a threshold…"*

11. L460-463, "The signals … TD techniques." How much improvement compared to other techniques? Did other techniques also use PEG?

While an exact numerical comparison is not available, the improvement is demonstrated by the thermograms following a sigmoidal shape rather than a Gaussian shape, indicating smoother evaporation. PEG standards were also used with VIA, where steeper decreases beyond T_{max} were observed, suggesting higher fragmentation or losses within the interface (Zhao et al., 2024).

12. Figure S14, please provide references for the FIGAERO data.

The reference is added

13. L485-486, "Longer residence … values." I think this should be the opposite. Shorter residence time particles might not reach thermal equilibrium, so they need a higher temperature to evaporate completely.

We would like to thank the reviewer for pointing out this error. The plot labels were corrected, and the text was revised. 60 ms represents the residence time with a sample flow rate of 0.75 SLPM and hot flow rate of 0.25 SLPM, while 72 ms represents the time with 1 SLPM sample flow rate and 0.25 SLPM hot flow rate.

Lines 513 – 516: *"Longer residence times allow for gradual heating and equilibration, leading to lower temperature values. In contrast, shorter residence times accelerate desorption, resulting in higher temperature values due to insufficient thermal equilibration."*

SI Figure S15: "*Figure S15. Effect of the residence time inside the TD region on the T_{max} corrected T_{50} values for PEG. 72ms represents a sample flow rate of 0.75 SLPM and HF of 0.25 SLPM, while 60ms represents SF of 1 SLPM and HF of 0.25 SLPM."*

14. Figure 7: I don't understand the purpose of this figure since you did not show any of your data.

Figure 7 presents the T_{50} values determined using WALL-E and illustrates how different volatility estimation methods lead to varying predictions. This framework helps visualize the uncertainty across methods and, based on the highlighted regions, allows us to estimate the volatility class a measured compound would fall into.

15. Figure 8: Is the mean line showing the average of heat and cool? It is not clear to me how you used the data from the fast cool ramp.

We applied the sigmoid fitting method to both the heating, cooling, and fast cooling ramps, extracted the T_{50} values from each, and averaged them. The orange line represents the averaged T_{50} value.

Lines 549-554*: "Figure 8: Comparison of estimated T_{50} values for α-pinene derived SOA compounds, specifically $C_{10}H_{16}O_{6\text{-}9}$ with volatility predictions from COSMO-RS and SIMPOL models. The measured T_{50} values (orange) are shown with their min/max range, while the shaded regions represent model predictions taking into consideration the isomerisation. We*

applied the sigmoid fitting method to both the heating, cooling, and fast cooling ramps, extracted the T_{50} values from each, and averaged them. The orange line represents this averaged T_{50} value."

16. L535-537, "By using … 1 ug m-3)." I am not fully getting this. Where did you show these results?

Concentrations were estimated based on the declustering method discussed in this work. Hence, we determined the concentration of individual SOA compounds. As shown in Figure R1, the products present in α-pinene-derived SOA range from ~10 pg m^{-3} to 70 ng m^{-3} for a total SOA mass of 1 µg·m^{-3} measured by the SMPS.

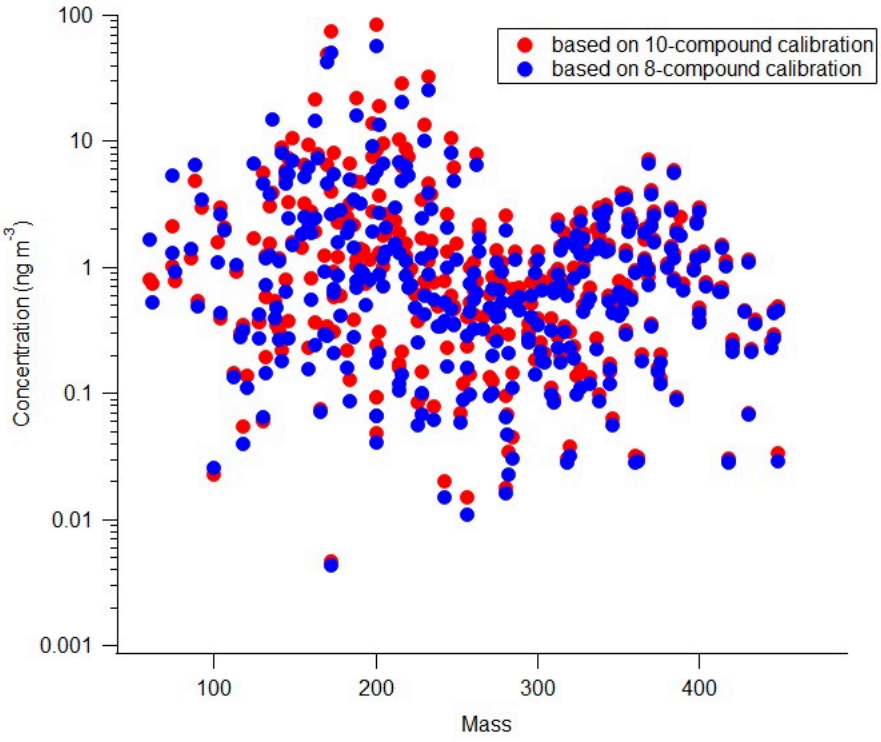

Figure R1. Product concentrations of individual α-pinene-derived SOA compounds were quantified using the declustering procedure using the 8- and 10-compound calibration solution. Total SOA mass of 1 µg m^{-3} was measured by an SMPS.