Response to reviewer

We thank the reviewer for the time and efforts spent on our manuscript and particularly for the valuable suggestions and comments that helped us improve the manuscript. We provide below point-by-point responses to the reviewers' comments and indicate how we implemented the changes suggested by the reviewers in the revised manuscript (blue text), with the reviewer' original comments in ***italic and bold***.

This manuscript (Manuscript ID: egusphere-2025-5655) presents an original and timely investigation into the widespread occurrence of large molecular methylsiloxanes in ambient aerosols. The topic is both novel and important, as it highlights a previously underrecognized group of synthetic organic compounds within atmospheric particles. The multidisciplinary approach, combining measurements from diverse environments with detailed chemical characterization, is a significant strength of the study. The results are convincing and suggest that these compounds may play a more substantial role in atmospheric chemistry than previously appreciated. Overall, the work represents a valuable contribution to atmospheric chemistry and aerosol science, and I recommend publication after minor revision.

Here are some comments in details:

The term "large molecular methylsiloxanes" is central to the study but is currently used somewhat broadly. Please provide a clearer operational definition in the Methods section, including typical molecular weight ranges and the key diagnostic ions used for mass spectrometric identification.

Response: We have expanded the Methods section to provide a clearer operational definition of "large molecular methylsiloxanes". Based on prior thermal tests of PDMS with different molecular weights (Yao et al., 2023), PDMS with a viscosity of 10 cSt, dominated by molecules containing approximately 15 siloxane units (with characteristic ions at m/z = 1110 for cyclic species), exhibits its main desorption/decomposition peak slightly below 200 °C. In contrast, higher-molecular-weight PDMS (e.g., 20 cSt, ~25 siloxane units) shows its dominant peak above 200 °C. Moreover, methylsiloxanes containing ~15 siloxane units have extremely low volatility under ambient conditions. Therefore, we

suggest ~15 siloxane units and 200 °C as practical thresholds for defining large molecular methylsiloxanes. This definition is now explicitly stated in the Methods section.

"Based on prior thermal tests of PDMS with different molecular weights (Yao et al., 2023), PDMS with a viscosity of 10 cSt, dominated by molecules containing approximately 15 siloxane units (with characteristic ions at m/z = 1110 for cyclic species), exhibits its main desorption/decomposition peak slightly below 200 °C. In contrast, higher-molecular-weight PDMS (e.g., 20 cSt, ~25 siloxane units) shows its dominant peak above 200 °C. Moreover, methylsiloxanes containing ~15 siloxane units have extremely low volatility under ambient conditions. Therefore, we suggest ~15 siloxane units and 200 °C as practical thresholds for defining large molecular methylsiloxanes." (Page 4, Line 116–121)

While the study benefits from data collected at multiple sampling locations, it would be helpful to comment briefly on how representative these sites are of broader regional or global conditions. A short discussion of potential sampling biases (e.g., proximity to emission sources, meteorological influences) and the expected variability of methylsiloxane mass fractions across seasons and regions would strengthen the manuscript.

Response: We have expanded the Discussion section to comment on the representativeness of the sampling sites and potential sampling biases. The samples analyzed in this study primarily originate from Europe and South America, and therefore may not fully capture the variability of methylsiloxane mass fractions in other regions such as Asia, Africa, or North America, which require further investigation. In addition, Lithuania has a relatively small geographic extent, with urban, coastal, and forested areas located in close proximity, which may lead to overlapping influences from multiple emission sources and meteorological transport. These limitations and their implications for regional and seasonal variability are now briefly discussed in the revised manuscript.

"It should be noted that the samples analyzed here primarily originate from Europe and South America, and may not capture methylsiloxane variability in regions such as Asia, Africa, or North America. Additionally, Lithuania's small geographic size, with urban, coastal, and forested areas in close proximity, may result in overlapping influences from multiple emission sources and local meteorology." (Page 15, Line 392–395)

Line 21: The manuscript states that methylsiloxanes constitute 2.0–4.3% of the "non-refractory organic aerosol mass". Please clarify that this percentage refers specifically to the non-refractory organic component and acknowledge that refractory or less

volatile compounds are not included. A brief explanation would improve the transparency of the interpretation.

Response: We thank the reviewer for this suggestion. The Methods section already addressed this issue, and we have now added additional details for clarity.

"In addition, we focused on the desorbed organic aerosol fraction up to 350 °C, hereafter referred to as non-refractory organic aerosols (OA). We did not investigate the non-desorbed fraction due to the technical limitation of our custom-designed heating unit. Previous work has shown that large molecular methylsiloxanes, such as PDMS with 10,000 cSt and 800 siloxane units, can withstand temperatures exceeding 650 °C (Yao et al., 2023). Consequently, part of the large molecular methylsiloxanes may not have undergone complete thermal decomposition in our experimental conditions, and both methylsiloxane and total organic aerosol concentrations reported here should be considered lower-bound estimates." (Page 4, Line 122–127)

Line 70: "the Hague" should be corrected to "The Hague".

Response: Corrected.

Line 74: "pre-backed" should be revised to "pre-baked".

Response: Corrected.

Line 139: "methylsilxanes" should be corrected to "methylsiloxanes".

Response: Corrected.

Line 155: Please add the preposition "at" after "occurring".

Response: Revised.

Line 187: Replace "was" with "were".

Response: Corrected.

Line 192: The phrase "60–90% lower" appears inconsistent with the numbers presented and should be revised to "10–40% lower".

Response: Revised.

Line 234: The statement "traffic currently recognized as their only known source" is overly absolute. Please rephrase to acknowledge the possibility of additional or emerging sources.

Response: Revised.

"with traffic currently recognized as their only known source (additional sources cannot be excluded)" (Page 10, Line 240)

Line 345: The phrase "three to four orders of magnitude lower than the methylsiloxane intakes in urban and coastal regions" risks overgeneralizing all urban and coastal environments. Consider qualifying this comparison more carefully.

Response: Revised.

"in urban and coastal regions reported in this study" (Page 14, Line 352)

Line 411: Replace "may exceed that of other synthetic compounds" with "may be comparable to or exceed that of other synthetic compounds" for greater accuracy.

Response: Revised.