Response to reviewer comments for manuscript: “The saturation vapor pressures of higher-order polyethylene glycols and achieving a wide calibration range for volatility measurements by FIGAERO-CIMS”

Ylisirniö et al.,

We thank the reviewer for their constructive comments regarding our manuscript. Below we will address the specific issues point by point. The reviewer’s comments are in black and our answers are in blue.
Reproduced changes to the Manuscript or Supplement Information are highlighted in red.
Line numbers before the red response text refer to line numbers in the modified manuscript.

We also made small corrections and improvements to the flow of the text which are not shown here.

Reviewer 2:

The study discusses calibration of the saturation vapor pressures of the FIGAERO-CIMS using the PEGs. The size range of the PEGs employed for the study was maximally up to PEG-15. Employment of the wide range of sizes of PEGs is the key novelty of the study. Since the experimental data for saturation vapor pressure of the PEGs with large sizes are unavailable, the authors employed various types of numerical approaches for estimating it. The desorption temperature of the PEGs was related with saturation vapor pressures using an empirical equation. The experiment was conducted sufficiently carefully. The manuscript is well-organized, and easy to follow. I suggest publication of this manuscript after the authors address the following comments.

Temperature and saturation vapor pressure

The FIGAERO-CIMS retrieves volatility by heating the sample. I believe that standard temperature for saturation vapor pressure for the study would be around 20–25 °C, while desorption temperature is much higher. For relating desorption temperature with saturation temperature, enthalpy for evaporation (Delta_H) of the calibrants and actual samples would play important roles. It would be great if the authors could explain why desorption temperature of the PEGs could be related with volatility of atmospheric (relevant) organic matter in more detail.

The reviewer raises an important and interesting question here: how accurately measurement results for PEGs can be related to results for actual organic aerosol, especially given that experimental desorption temperatures are much higher than the standard temperature for saturation vapor pressure (here we used 25 °C). Addressing this issue comes down to two relationships and how adequate our assumptions are for them: (a) the temperature dependence of ΔH, and (b) the relationship between saturation vapor pressure (or C*) and ΔH.

Regarding (a), we assumed $d\Delta H/dT = -0.1\ \mathrm{kJ\ mol^{-1}\ K^{-1}}$, the same value used for PEGs by our main reference study (Krieger et al., 2018), and well inside the range of values reported for various organic acids with better atmospheric relevance (Bilde et al., 2015; Riipinen et al., 2007; Tong et al., 2004) and found by Epstein et al., (2010) to apply to a broader range of organic species within uncertainties (at least up to 200 kJ/mol). Furthermore, we found that the uncertainties of our own experimental and fitting methods (e.g., as shown in Fig. S2) are similar to the variability of our results when we adjusted dΔH/dT even by 100% (to 0 or -0.2 kJ mol^{-1} K^{-1}; not shown).

As to not to distract much, we only added a sentence to the manuscript relating to (a), along with the cited references.

Line 363:

Here, we used a temperature dependence of $d\Delta H/dT = -0.1$ kJ mol^{-1} K^{-1} as a rough literature-based estimate (Krieger et al., 2018), but which is similar to dependences found also for a broader range of organic compounds (Bilde et al., 2015; Epstein et al., 2010; Riipinen et al., 2007; Tong et al., 2004).

Regarding (b), a well-established estimate for ΔH(C*) (at 25 °C) for a broad range of organic compounds was derived by Epstein et al. (2010), which we reproduce in Fig. S2 (solid gray line). Compared to our findings for PEGs (and also those by Krieger et al., 2018), the Epstein relationship predicts somewhat higher values for ΔH: by up to ~20 kJ/mol (Fig. S2). Again, our uncertainties are typically higher than that, but the offset is persistent and we thus believe real. Also, considering the untypical structure of PEGs compared to more atmospherically relevant organics, such a discrepancy would not be surprising. A compound with a certain C* and higher ΔH will exhibit a lower experimental T_{max} than a compound with the same C* but a lower ΔH. Consequently, C^* values assigned to organics that follow the Epstein relationship will be overestimated, when assigned based on a T_{max}-C^* relationship established for PEGs.

We added a comparison between PEG results and new model calculations using the Epstein relationship in a new Fig. S3, illustrating the overestimation that could be incurred by that issue. The bias increases with decreasing C* to up to about an order of magnitude at ELVOC and ULVOC ranges. The issue is also discussed in a new paragraph in the Conclusions chapter.

Line 565:

"An additional error source for practical applications of a T_{max}-C^*-relationship established via PEGs is likely due to the relatively low ΔH values we find for PEGs (in agreement with Krieger et al., (2018)), when compared to broader sets of organic compounds (Figure S2). As illustrated in Figure S3, this discrepancy may induce overestimations for C^* assigned based on T_{max} measured for more typical organics but using a T_{max}-C^* relationship established for PEGs. As ΔH is of increasing importance with increasing desorption temperature, the expected average bias increases with decreasing C^*, up to about an order of magnitude in the ELVOC and ULVOC ranges."

Figure S3:

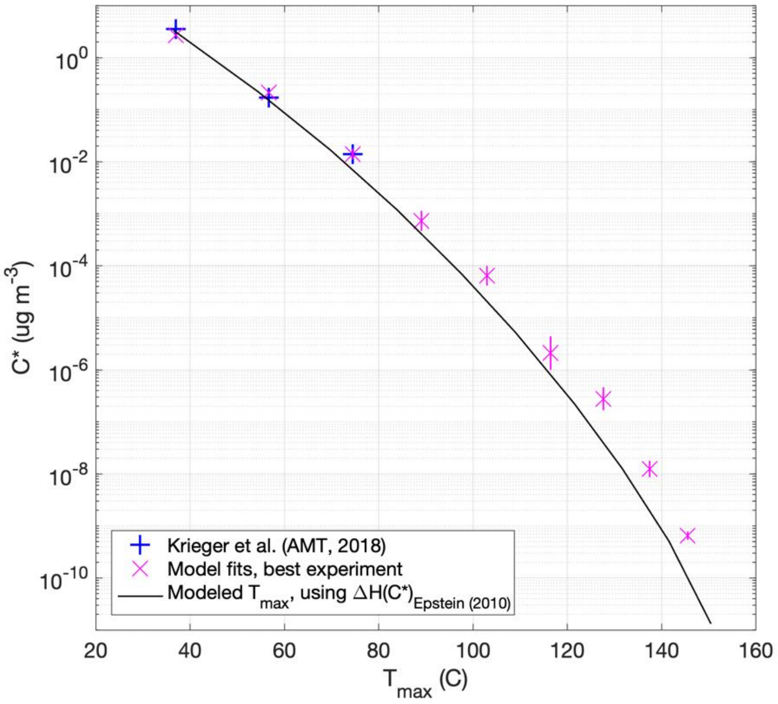

Figure S3: Markers present saturation vapour concentrations C^* for PEGs, at 298 K, using datasets and colour coding as described in Figs. S1 and S2, versus the T_{max} as obtained during the best-fitting experiment (see Fig. S1 for details). The black line presents model simulation results for T_{max} using a series of C^* values in the same range, but using ΔH values obtained via ΔH [kJ mol^{-1}] = 131 – 11 log$_{10}$(C^* [µg m^{-3}]), as proposed by Epstein et al. (2010) based on a broad set of organic compounds. The discrepancy between the line and the markers suggests that if ΔH for PEGs are relatively low (cf. Fig. S2), C^* values assigned to organics that follow the Epstein relationship will be overestimated, when assigned based on a T_{max}-C^* relationship established for PEGs. This positive bias increases here with decreasing C^*, up to about an order of magnitude.

Typos and grammatical issues

There are some typos and grammatical issues with the manuscript. It may be a good idea to use a software or an online tool for checking the manuscript.

Thank you for pointing this out. Improvements have been made to whole manuscripts.

References:

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