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 1:

General Comments

This study addresses the important challenge of calibrating the FIGAERO-CIMS instrument for measuring the volatility of organic aerosol (OA) constituents, particularly for extremely low-volatility compounds (ELVOCs). Current calibrations typically rely on polyethylene glycols (PEGs) up to PEG-9, which limits the lower end of the volatility range. The authors extend this range by including PEGs up to PEG-15, thereby significantly improving calibration coverage.

The experiments are thoroughly conducted, with desorption temperatures (Tmax) carefully measured and reported. The authors also compare a comprehensive range of methods for estimating the vapor pressure (C*) of PEGs. The experimental results, vapor pressure estimates, as well as the discussion, provide valuable insights—not only for FIGAERO-CIMS users but also for the broader community using thermal desorption-based volatility measurements.

I strongly recommend the manuscript for publication, but I have a few comments and suggestions for clarification and improvement:

Specific Comments

(1) The conclusion regarding the linearity between C* and PEG number is somewhat misleading. A linear relationship should not be expected, and in fact, non-linear behavior is well documented in various parameterizations (e.g., L2016, S2018, M2019 in this study). In addition, different conformers of the same PEG molecule can exhibit varying intermolecular interactions, leading to different saturation concentrations. This is actually illustrated in Figure 1: the best-performing estimation methods (desorption model, COSMO-RS, MGM) show that C* values for larger PEGs tend to be non-linear and above the dashed line, contrasting with other parameterization methods.

Instead, the relationship between C* and the measured Tmax is more dir. ect. In Figure 2, when considering the uncertainties in C* (as shown in Figure 1), the linear fit is not significantly worse

than other fits.

The reviewer is correct that true linearity should not be expected when considering decrease of volatility with increasing PEG-number (and so effectively molecular mass). We have therefore modified the text discussing this effect.

Line 305:
"Almost all used models estimate a broadly log-linear decrease in volatility (C*) when compared against PEG-number (Figure 1a), except for COSMOtherm, MGM and to some degree the desorption model, which both estimate higher volatilities than just linear extrapolation from literature data. Note that although many models appear to estimate loglinear decrease in volatility vs PEG-number (and thus molecular mass), true linearity should not be expected, as has been pointed out in previous studies (Li et al., 2016; Mohr et al., 2019; Stolzenburg et al., 2018). When comparing the estimated C* results to measured Tmax (Figure 1b), the relationships appear only log-linear for the smaller PEGs but turn out roughly log-polynomial over the full range of PEGs 5-15. This effect is further discussed in next the section."

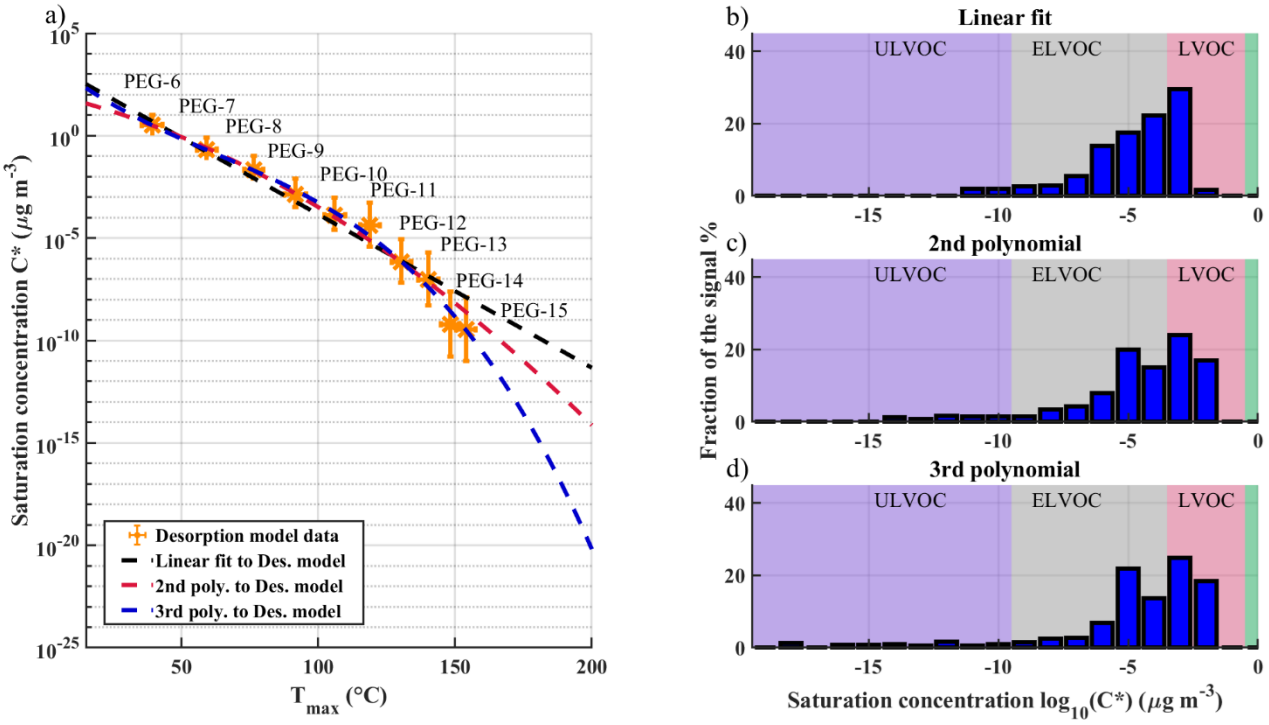
We also toned-down assertions of log-linearity in various places in the manuscript, where they were likely too strong or not justified.

When regarding the relationship between C* vs Tmax, we however disagree that a linear fit would perform as well as polynomial fits, especially when estimating volatilities in the lower LVOC and ULVOC range ($\log(C^*) < -6$). To illustrate this, we modified Figure 2 so that all fits are now fitted to desorption model data and resulting VBS distributions are modified to match this. Figure 2a now also contains error bars along both x and y-axes. The linear fit takes into account both x- and y-axis uncertainties and all fits take into account the uncertainty in the desorption model C* estimates. Although all three fits broadly agree up to $\log(C^*) < -6$ / $T_{max} < 130$ °C, the polynomial fits estimate much lower volatilities than the linear fit for higher Tmax values. These results support our conclusion that polynomial or other non-linear functions are better-suited for calibration fits across wide temperature ranges. We also added additional text to line 329, pointing out alternative methods for the line fitting. Most of these methods are readily available in common data-analysis languages used in aerosol science, such as Matlab, Python, R and IGOR Pro.

Line 328:

"Besides Gauss-Markov estimation, Weighted Least Squares regression, Orthogonal Distance Regression or Bayesian regression can be used for fitting polynomials with uncertainties."

New Figure 2:



Furthermore, it is somewhat confusing that the Tmax values in Figures 1 and 2 are taken from two measurements (presumably A and B?), but C* from the desorption model is the averaged value from A, B, and C. Would it not be better to use the average T_max from all three measurements (A, B, and C) for consistency? Also, I am curious about the uncertainty of Tmax, which is not clearly mentioned.

The reviewer has a good point about the consistency. However, using average of all available measurements of Tmax would not give realistic mean value as measurements A, B and C were all using different ramping rates, namely A = 15min ramp time, B = 5min ramp time and C = 10min ramp time, which has been reported to shift Tmax values. The reviewer however has good point that used Tmax values should be reported and therefore we have added the mean value and standard deviation of measurements A to end of Table S3 and modified the text as follows.

Line 292:

"For the sake of clarity, the shown T_{max} values are average values from experiment A, as each experiment used different ramping rates, which affect the measured T_{max} values. Results from desorption modelling are averages over a set of measurements as described in Section 3.3. All shown volatility results are also displayed in Table S2 (in terms of P_{sat}) and S3 (in terms of C^*) in the supplemental material. Table S3 also shows the used T_{max} values and their standard deviations."

New line in Table S3

Average T_{max} values + std shown in Figure 1 and Figure 2.	21.3 ± 2.05	39.2 ± 3.74	59.16 ± 3.6	76.36 ± 3.45	91.62 ± 3.83	106 ± 3.74	118.87 ± 3.74	130.4 ± 3.62	140.29 ± 3.71	148.17 ± 3.41	153.94 ± 3.66

(2) Please clarify whether the reported mass loading refers to individual compounds or the total mass, and maybe more important which one is more essential or more related to Tmax. It is unclear whether low mass loading (< 105 ng) could influence Tmax. If this is a potential factor, it should be discussed.

Reported mass loading refers to total collected aerosol mass. This is now clarified in the text as shown below. Mass of individual compounds ranged from 5-10 ng per compound, depending on the experiment.

Line 120:
"Note that the mentioned aerosol mass loadings refer to total collected mass over all PEG compounds. Collected masses of individual PEGs ranged from ~5 to 10 ng per compound."

While mass loading does have clear impact on the determined Tmax value, in effect that higher mass loadings tend to shift the observed Tmax values to higher temperatures, we have not noticed nor it has been reported that too low mass loading would have an effect on Tmax, as long as observed CIMS signals are not too noisy or below detection limit.

Technical Comments

Line 21: It's unclear where the "150 °C" value comes from. This is described more clearly in Lines 75–76. Please ensure consistency across the manuscript.

Text have been modified, and some references added, to clarify this as follows:
Line 21:
… OA constituents measured from lab generated or ambient aerosols routinely reach up to 160 ºC (Z. Li et al., 2021; Masoud et al., 2022)..."

Line 35: Instead of "now-known," consider using "best-estimated" for clarity and specificity.

Text is modified as requested.

Line 77: The sentence suggests methods were used to improve measurement accuracy. It would be more accurate to say that different methods were used to improve the prediction of vapor pressures.

The reviewer has a valid point. The sentence has been modified as follows:
Line 78:
We utilize a combination of different methods to improve the accuracy of estimating saturation pressures of low volatility compounds.

Line 159: Remove "experimental".

Text corrected as requested

Figure S1: It is unclear how the uncertainties for the magenta crosses were derived. The legend notes that the yellow crosses represent the model fits of C* (rather than ΔH) to experiments.

We apologize for the unclear notations in the legends of Figs. S1 and S2, in particular the references to "ΔH (T)", which was merely meant to indicate that ΔH itself was assumed to depend on temperature. But in the course of the work, that assumption became the default that we used throughout (as described in Section 3.3). Hence, we now removed those references in the legends. In all cases of yellow and magenta crosses, the results show model fits of both C* and ΔH to the experimental measurement results.

Regarding the uncertainties for the magenta crosses, they are now explicitly explained in the caption of Fig. S1 (and which is then referenced in the caption of Fig. S2).

Added text to Fig. S1 caption:

"Magenta crosses, also with uncertainties as vertical lines, are the results for the best-fitting experiment (described as "Experiment A" in the main text; uncertainties in this case correspond to the standard deviation, in logarithmic space, of those of the 24 optimizations resulting in an f within a factor of 2 of f^*)."

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 $d\Delta H/dT = -0.1$ 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 (Tong et al., 2004; Riipinen et al., 2007; Bilde et al., 2015) 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 $d\Delta H/dT$ 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 (Tong et al., 2004; Riipinen et al., 2007; Epstein et al., 2010; Bilde et al., 2015).

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:

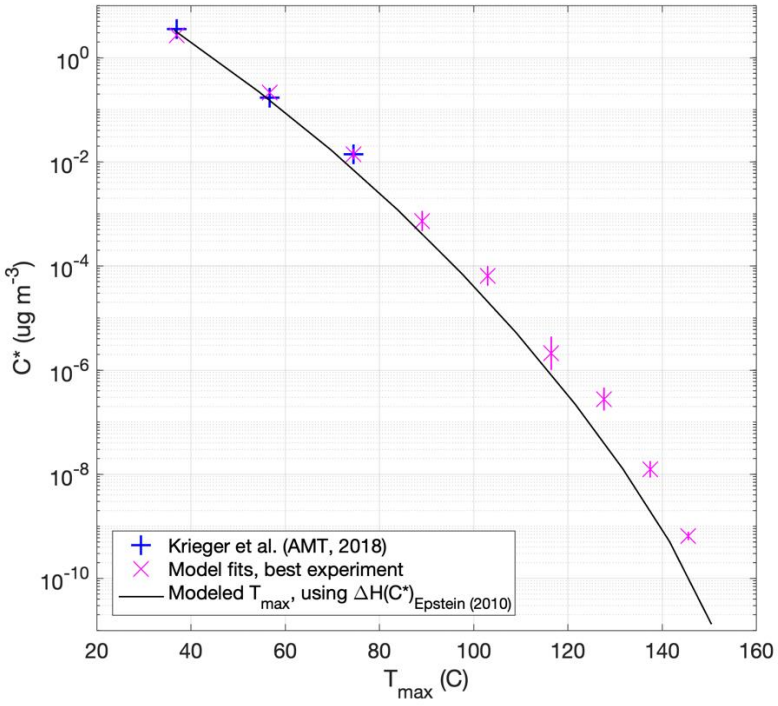


Figure S3: Markers present saturation vapour concentrations C^* for PEGs, at 298 K, using datasets and colour coding as described in Figs. S1 and S2, versus the T_{max} as obtained during the best-fitting experiment

(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.