Responses to reviewer's #1 comments

General Comments

Jackson et al. provides volatility measurements for a set of 6 pesticides in current use through application of a filter desorption method utilizing the Filter Inlet for Gases and AEROsols coupled to an iodide mode Chemical Ionization Mass Spectrometer (FIGAERO-CIMS). The authors discuss broad variability and inconsistency in measured and reported vapor pressures (volatility) for many compounds, dependent on measurement method. FIGAERO-CIMS volatility is derived from a relationship between temperature of maximum thermal desorption signal (Tmax) and volatility (increasing Tmax indicates lower volatility). This relationship is quantified by calibration of the technique against a set of polyethylene glycol (PEG) polymers of different lengths, which can be loaded onto the filter by syringe deposition or atomization. This calibration is then utilized to assess the volatility of the target pesticides when they are atomized in a mixture or individually.

Jackson et al. conclude that, in agreement with prior literature, use of a syringe for calibrant or sample delivery is less effective than atomization. However, as noted in specific comments below, greater consistency is achieved between literature PEG Tmax values using the syringe method than atomization. While arguments from prior literature are used to highlight the unsuitability of the syringe method, the data as presented does not provide clarity as to why syringe delivery is unacceptable. Additional quantification of thermogram peak width and subsequent resolution or overall variability of each measurement method would provide valuable insight into the failings of the syringe method for PEG calibration.

We'd like to thank Referee 1 for their positive comments and to respond to the general and detailed comments as follows (reviewer comments in black and our responses in blue; the line numbers referred throughout are referring to the original manuscript). An updated version of the manuscript detailing the amendments from all of the reviewers comments is also provided.

In response to the general comment, the authors would like to clarify the argument presented in this paper regarding the syringe and atomisation method. It is not that the syringe an unacceptable method. Instead, we present the atomisation method as a more suitable method to be used in this study due to the following. Most importantly, the size of the calibration droplets on the FIGAERO filter need to be similar to those of the material being sampled for the calibration to be representative, in order to control this the atomisation method is required, in which a number of small droplets are deposited on the filter, compared to one large droplet when the syringe method is used. As pointed out by Ylisirnio et al. this is due to complete evaporation of a single compound of a given volatility from the filter during the thermal ramp being dependent on the size of the particle (due to varying surface-volume ratio). A molecule in the larger droplet from the syringe method takes more energy to evaporate in comparison to the smaller droplets on the filter in the atomisation method and therefore full evaporation takes longer. This results in the Tmax compound of the same volatility being higher in the syringe method and the overall thermograms being broader (as observed in figure 2 and backed up by the gaussian fits provided in S1). Secondly, the atomisation method presents a more relevant method compared to online sampling in the field and thus provides an opportunity to compare against results if required. Finally, the syringe method delivers a larger volume of material and this risks contamination of the mass spectrometer – see later discussion of the peak shapes. Overall, the atomisation method is the optimum method for sample delivery to the FIGAERO. In the amendments throughout the paper, we hope the reviewer is able to further appreciate the requirement for this calibration . To address this in the paper the following has been added to the end of the PEG discussion section (4.1)as an overview of the section: ' *Overall, the atomisation method was chosen since it was recommended in the previous literature and shown (S1 and S2) to be more repeatable and*

representative than the syringe method and lead to far less low volatility material entering the mass spectrometer, reducing the contamination'

Additionally, we must make the reviewer aware that it is only suitable to compare the data from the same apparatus and the particles measured are the same size. In addition, this means that any calibration must have the same particle size as the compounds of interest (e.g pesticides) as the size of the compound impacts the volatility in the atomisation method.

Repeats of thermograms of representative PEGs covering the atmospherically relevant volatility range are presented and provided in the supplementary as part of the gaussian fits which is accompanied by the standard deviation and full width half maximum of each peak, this aims to provide clarity on the repeatability of the experiments and the gaussian fit of the thermograms. An example of the summary tables provided in the supplementary material is shown below:

Supplementary Table 1: Presented standard deviation and full width half maximums for each of the pesticide atomisation thermograms.

Compound	Run Number	Standard Deviation	Full Width Half Maximum
2,4-D	Pesticide run 1	0.187182	18.1
Dicamba	Pesticide run 1	0.241627	16.3
MCPA	Pesticide run 1	0.163907	15.9
Mesotrione	Pesticide run 1	0.196694	18.5
Mecoprop-P	Pesticide run 1	0.207007	20.6
Trilfuralin	Pesticide run 1	0.202343	44
2,4-D	Pesticide run 2	0.074938	36.5
Dicamba	Pesticide run 2	0.194977	58.9
MCPA	Pesticide run 2	0.163907	16
Mesotrione	Pesticide run 2	0.320658	41.3
Mecoprop-P	Pesticide run 2	0.207007	21
Trilfuralin	Pesticide run 2	0.271879	n/a

The above text gives an overview of the comments presented by the reviewer. More specific answers are provided below.

Pesticide volatilities are measured and reported for 6 pesticides of interest and compared to literature values, as well as values derived from 2 structure-activity relationship models. Here, Jackson et al. show close agreement between literature and FIGAERO-measured values for Dicambia, MCPA, and MCPP. Volatility of 2,4-D is measured as more than 1 order of magnitude higher than the literature value, explained here by differences in the PEG calibration particle size distribution. Volatility of mesotrione is measured as more than 2 orders of magnitude lower than the literature value, explained by error in the measurement of said literature value (measurement conducted at a higher temperature than this study). A Clausius-Clapeyron relationship is used to argue that observed and modeled volatilities are reasonable given the temperature difference between the two measurements. Trifluralin is noted as the highest volatility pesticide measured here. However, as noted in specific comments below, the data shown in Figure 6 seems to contradict this, since the Tmax observed there is substantially higher than the 27.7C reported in Figure 7. Furthermore, the desorption profile of Trifluralin has a uniquely large right tail and further assessment and analysis of this species behaviour would be appreciated.

We thank the reviewer for the comment. The plotting of the graph was revisited, and the incorrect temperature had been plotted, this has been amended and updated below. We greatly appreciate the referee spotting this error. The tail can be explained by the high concentration of pesticide injected onto the FIGAERO and sampled into the CIMS, resulting in the compounds coating the IMR and coming off over time. As Trifluralin is relatively volatile (compared to the other pesticides introduced into the CIMS), it will quickly re-evaporate, creating the tail. The other pesticides on the other hand will re-evaporate on timescales longer than that of a thermogram and so will be observed by an increase in background over the course of multiple experiments. At the start of each experiment, it was ensured that each of the pesticide signals returned to background levels before a new experiment was begun, as well as making sure the filter has properly cooled down to make sure no initial evaporation of Trifluralin occurs before the start of the experiment and thus the initial peak portion of the experiment is unaffected by the tail. To improve clarity of this issue a discussion should be added to a revised manuscript to say the following: '*The tail observed in the Trifluralin peak is due to the large concentration of pesticides injected into the mass spectrometer, leading to some residue being present in the IMR which can then re-evaporate creating a tail. This is not visible for the other compounds measured as they are of lower volatility and therefore would expect to remain on the walls of instrument for longer than the time taken for a single thermogram, potentially coming off in the background over time.'*

Generally, Jackson et al. concludes that FIGAERO-CIMS measurements of volatility are valuable additions to pesticide environmental assessment to understand the fate of toxic pesticides in the environment. Such measurements can improve modeling of fate and transport and environmental persistence. The manuscript presents a unique set of measurements of a particular set of pesticides as an example of this technique and its reasonable agreement with other vapor pressure measurements. Furthermore, the manuscript identifies a series of key concerns in the vapor pressure measurement space, including poor documentation of measurement methodologies including temperature measurement.

The manuscript would benefit from additional quantification when making comparisons between measurements and measurement techniques, both in terms of quantified Gaussian goodness of fit and peak shape metrics, and in terms of presenting uncertainty in the form of standard deviations or propagated error. Furthermore, additional literature comparisons where possible would be valuable. As discussed in the technical comments, small updates to the presented figures would improve legibility, consistency, and clarity across the manuscript.

Overall, the manuscript provides a unique measurement of pesticide volatility and is an informative first step toward building a more consistent picture of pesticide fate and transport in the environment. I appreciate the author's consideration of this reviewer's comments and their ongoing work to illuminate this important area.

We'd like to thank Referee 1 for their general comments and especially appreciation for the requirements needed for this work and understanding in the importance of this topic area of both FIGAERO-CIMS and pesticide research. Responses regarding the clarity and legibility of the manuscript will be addressed in the final version and the authors appreciate the specific and technical comments made by the referee, all of which have been taken into consideration.

Specific Comments

Line 105-107: The authors describe how volatility measurements may be conducted at higher temperatures and be extrapolated to lower temperatures. However, later in the manuscript when discussing this effect with mesotrione, it seems that rather than being extrapolated to lower temperatures, the measurements at high temperatures are simply used at low temperatures (there is no particular extrapolation). The authors then describe using a Clausius-Clapeyron relationship as an

appropriate adjustment to vapor pressure. How widespread is the practice of ascribing high temperature vapor pressure measurements to low temperature conditions?

We would like to thank the reviewer for pointing out the lack of clarity regarding this topic. The literature values used for Mesotrione were provided as reference data from a safety case perspective for the approval of the use of Mesotrione. The basis of the arguments in the case are that if the vapour pressure is sufficiently low at the higher temperatures under the measured conditions, then the volatility of the pesticide will be even less at the ambient temperatures and so will not undergo significant transport (this is central to regulatory compliance). Rather than use the upper limit value that is applied for compliance purposes we have used a Clausius-Clapeyron approach to extrapolating the volatility to lower temperatures to show that the extrapolated value is consistent with our observations/. To improve the clarity of this the following text should be added to a revised version of the manuscript.

'*Previous studies of the vapour pressure value for mesotrione were determined at 373K of 5.7x10^{-6} Pa (Lewis et al., 2016) and so have been previously considered to be an upper limit value in regulatory framework literature (Efsa, 2016) since lower vapour pressures will occur at lower temperatures. We calculate the vapour pressure at 293K by extrapolating the Lewis et al data included in (Efsa, 2016) to 298K using a Clausius-Clapeyron relationship and compare it with our observation in figure 9 along with MGM model predictions and show consistency across both observations and models for Mesotrione.'*

Line 147-152: What are the implications of pesticides residing in a particular volatility class? What inference can you make about the fate and transport of that pesticide in the environment? Both here and elsewhere the authors comment on the volatility classes, but I think additional clarity in interpreting these classes would be valuable.

There are a number of implications of the volatilities of pesticides. The manuscript has been edited to state the following: '*The consequence of a pesticide having a higher volatility gives rise to the higher likelihood of a pesticide residing predominantly in the gas phase and thus less likely to undergo wet or dry deposition than a pesticide of lower volatility in the particle phase*.' Firstly, the phase at which it exists in in the atmosphere influences the potential for atmospheric transport or deposition, as well as the mechanisms of wet or dry deposition. If a pesticide is predominantly in the particle phase, then it is more likely to undergo deposition and less likely to be transported large distances from the source, whilst the opposite is more likely to be true if a pesticide is more volatile and thus more likely to exist in the gas phase. This understanding is required if we are to move to an atmospheric model of pesticide transfer through the air.

Line 165: Please note the thickness, pore size, and brand of the filter used in addition to the material. Similarly note purity and sources for all materials when described in the methods section.

The filters used were 25mm diameter and 2.0µm pore size PTFE filters purchased from Cobetter lab. This will be amended in the manuscript.

Line 167: In what sense is the filter "backflushed"? The flow direction of heated nitrogen is the same as the initial particle sampling flow. (This may just be a filter sampling terminology I am unfamiliar with!)

We thank the reviewer for highlighting this. This comment was also addressed by reviewer 2.. Reverse flushed refers to the process within the operation of the FIGAERO desorption method in which the nitrogen flow is heated and flowed onto the filter containing the compound of interest. In order to avoid confusion with the reader, a revised line now read '*The filter (and any particles on it) is*

flushed with nitrogen and continuously heated at a rate of 8.75°C min^{-1}.' This will be updated in further versions of the manuscript.

Line 178-179: Here the authors mention Bannan et al. (2019). I would suggest including PEG Tmax data from that study for comparison in addition to Ylisirnio et al. (2021). In general, I think the manuscript would benefit from a broader range of comparison to FIGAERO data sets where possible to better capture the variability in available measurements and the corresponding uncertainty in the measurement here.

The Bannan et al. (2019) paper was the first to use the PEG series to calibrate the FIGAERO CIMS Tmax data for volatility following on from the work of Krieger et al which details a range of methods to measure vapour pressure from PEG calibrations. However, the Bannan et al study used the syringe method, which Ylisrnio et al subsequently showed led to extended evaporation times of droplets on the filter. The important point here is that since the evaporation time of material of a given volatility from the filter is dependent on the size of the droplet on the filter the calibration curve that relates Tmax to volatility will be highly dependent on the droplet size as well as on the characteristics of the FIGAERO filter, the nitrogen flows and the temperature ramp rates. There is therefore no meaning in comparing Tmax v volatility calibrations from different instruments under different conditions with different sized droplets on the FIGAERO filter. We would go further and recommend that in order to derive volatility from the FIGAERO CIMS the calibration must be performed using the same system under the same conditions by depositing calibration particles with the same size distribution as the particles whose volatilities are to be determined.

Line 190: Was precisely 1 ug of atomized particles deposited on the filter for each measurement in this study based on live SMPS data?

We thank the reviewer for the comment. The 1ug of atomised filter was measured using equation 3 where c_{SMPS} is the average concentration measured by SMPS data during the experiment. The following has been added to an updated manuscript '*to ensure that 1µg mass was delivered onto the filter during each experiment, the sample time was determined using equation 3 by monitoring c_{SMPS}.during the course of each experiment'*

Repeatability: Were calibrations and measurements repeated in this study? I see that calibration measurements were repeated 3 times in the caption of figure 3. Please add to the body text as well. What is the distribution of measurements, and can uncertainty be represented by error bars on many of the figures here?

We thank the reviewer for the comment. Figure 3 contains error bars; however, the calculated errors are small and not particularly visible in the figure. The text has been updated to include this in the main body of the text. In addition to this, several runs have been added to the supplementary data to explore the repeatability of the thermograms which are accompanied by tables which include the standard deviation and full width half maximum of each thermogram (shown below in supplementary figure 1). From this we can see that the repeatability is good across the experiments in the atmospherically relevant portion.

Supplementary Table 2: Presented standard deviation and full width half maximums for each of the PEG syringe thermograms

Compound	Run Number	Standard Deviation	Full Width Half Maximum
PEG 1	PEG Syringe 1	0.043029	n/a
PEG 2	PEG Syringe 1	0.019841	n/a
PEG 3	PEG Syringe 1	0.061816	n/a
PEG 4	PEG Syringe 1	0.120898	n/a

PEG 5	PEG Syringe 1	0.141968	63.7
PEG 6	PEG Syringe 1	0.213258	652.4
PEG 7	PEG Syringe 1	0.249988	49.4
PEG 8	PEG Syringe 1	0.255238	46.9
PEG 9	PEG Syringe 1	0.267166	46
PEG 10	PEG Syringe 1	0.279353	45.3
PEG 11	PEG Syringe 1	0.279771	42.5
PEG 12	PEG Syringe 1	0.274312	42.1
PEG 13	PEG Syringe 1	0.264753	40.9
PEG 14	PEG Syringe 1	0.259454	40.7
PEG 15	PEG Syringe 1	0.227712	38.7
PEG 16	PEG Syringe 1	0.152519	n/a
PEG 1	PEG Syringe 2	0.055531	n/a
PEG 2	PEG Syringe 2	0.012884	n/a
PEG 3	PEG Syringe 2	0.070254	n/a
PEG 4	PEG Syringe 2	0.159831	n/a
PEG 5	PEG Syringe 2	0.158666	58.9
PEG 6	PEG Syringe 2	0.226129	51.6
PEG 7	PEG Syringe 2	0.287126	51.6
PEG 8	PEG Syringe 2	0.303555	49.4
PEG 9	PEG Syringe 2	0.307325	47.7
PEG 10	PEG Syringe 2	0.319395	48.3
PEG 11	PEG Syringe 2	0.329424	47.5
PEG 12	PEG Syringe 2	0.315942	n/a
PEG 13	PEG Syringe 2	0.278748	n/a
PEG 14	PEG Syringe 2	0.22262	n/a
PEG 15	PEG Syringe 2	0.150391	n/a
PEG 16	PEG Syringe 2	0.069654	n/a
PEG 1	PEG Syringe 3	0.080361	n/a
PEG 2	PEG Syringe 3	0.039363	n/a
PEG 3	PEG Syringe 3	0.140204	n/a
PEG 4	PEG Syringe 3	0.231058	n/a
PEG 5	PEG Syringe 3	0.22881	34.9
PEG 6	PEG Syringe 3	0.219188	32.4
PEG 7	PEG Syringe 3	0.24527	32.6
PEG 8	PEG Syringe 3	0.253734	35
PEG 9	PEG Syringe 3	0.276235	34.3
PEG 10	PEG Syringe 3	0.285409	34.2
PEG 11	PEG Syringe 3	0.291096	31.2
PEG 12	PEG Syringe 3	0.242444	25.5
PEG 13	PEG Syringe 3	0.158333	n/a
PEG 14	PEG Syringe 3	0.203823	n/a
PEG 15	PEG Syringe 3	0.064268	n/a
PEG 16	PEG Syringe 3	0.033518	n/a

Supplementary Table 3: Presented standard deviation and full width half maximums for each of the PEG atomisation thermograms

Compound	Run Number	Standard Deviation	Full Width Half Maximum
PEG 1	PEG Atomisation run 1	0.003731	n/a
PEG 2	PEG Atomisation run 1	0.027495	n/a
PEG 3	PEG Atomisation run 1	0.173071	n/a
PEG 4	PEG Atomisation run 1	0.063222	n/a
PEG 5	PEG Atomisation run 1	0.188054	n/a
PEG 6	PEG Atomisation run 1	0.214379	31.6
PEG 7	PEG Atomisation run 1	0.223407	31.7
PEG 8	PEG Atomisation run 1	0.22717	31.7
PEG 9	PEG Atomisation run 1	0.247393	35.1
PEG 10	PEG Atomisation run 1	0.277645	42.5
PEG 11	PEG Atomisation run 1	0.308204	51.2
PEG 12	PEG Atomisation run 1	0.298668	50.5
PEG 13	PEG Atomisation run 1	0.249717	45.4
PEG 14	PEG Atomisation run 1	0.183889	43
PEG 15	PEG Atomisation run 1	0.089173	37.4
PEG 16	PEG Atomisation run 1	0.031918	n/a
PEG 1	PEG Atomisation run 2	0.065051	n/a
PEG 2	PEG Atomisation run 2	0.11932	n/a
PEG 3	PEG Atomisation run 2	0.134942	n/a
PEG 4	PEG Atomisation run 2	0.195675	n/a
PEG 5	PEG Atomisation run 2	0.170252	42.2
PEG 6	PEG Atomisation run 2	0.234296	36
PEG 7	PEG Atomisation run 2	0.241734	33.4
PEG 8	PEG Atomisation run 2	0.216853	30
PEG 9	PEG Atomisation run 2	0.196929	30
PEG 10	PEG Atomisation run 2	0.181912	31.7
PEG 11	PEG Atomisation run 2	0.162213	35.8

PEG 12	PEG Atomisation run 2	0.15842	49.1
PEG 13	PEG Atomisation run 2	0.169465	n/a
PEG 14	PEG Atomisation run 2	0.149642	n/a
PEG 15	PEG Atomisation run 2	0.143715	51.7
PEG 16	PEG Atomisation run 2	0.172397	45.6
PEG 1	PEG Atomisation run 3	0.008783	n/a
PEG 2	PEG Atomisation run 3	0.051641	n/a
PEG 3	PEG Atomisation run 3	0.190573	n/a
PEG 4	PEG Atomisation run 3	0.033878	n/a
PEG 5	PEG Atomisation run 3	0.206966	n/a
PEG 6	PEG Atomisation run 3	0.203647	29.8
PEG 7	PEG Atomisation run 3	0.209143	28.7
PEG 8	PEG Atomisation run 3	0.213781	27.9
PEG 9	PEG Atomisation run 3	0.214382	28
PEG 10	PEG Atomisation run 3	0.221895	29.6
PEG 11	PEG Atomisation run 3	0.255236	34.5
PEG 12	PEG Atomisation run 3	0.311995	43.1
PEG 13	PEG Atomisation run 3	0.306441	41.2
PEG 14	PEG Atomisation run 3	0.209504	n/a
PEG 15	PEG Atomisation run 3	0.13016	n/a
PEG 16	PEG Atomisation run 3	0.06895	n/a

Methodology: Why were separate calibration and pesticide volatility desorptions necessary? Could PEG be included in the pesticide solutions and atomized simultaneously for a concurrent volatility calibration during pesticide desorption?

We thank the reviewer for the comment. Yes the PEG mix could be used and atomised simultaneously and it is appreciated that experimental biases involving differences in analyte and calibrant size distribution biases. In practice this increases complexity since PEGs may interact with the pesticides, the mass spectrum would be more complex. This also allowed the verification the volatility vs Tmax relationship in advance of conducting the pesticide experiments.

Line 249-250, "Conversely it is also important to determine the volatility of pesticides thought to be involatile (i.e., no chance of volatilization in the atmosphere) to ensure that there is no potential for atmospheric presence thus no further risk assessment in air is required.": Here, this argument is made the low volatility species have no atmospheric relevance. In other portions of the manuscript, the authors note that low volatility species can be sequestered in particles and avoid atmospheric oxidation and be transported long distances (Line 89) or that low volatility species can be resuspended in dirt or dust particles (Line 490). Is this line intended to capture the current state of environmental risk assessment policy? If so, that should be clear and distinct from the broader commentary the authors make on potential environmental fate based on the results of this study.

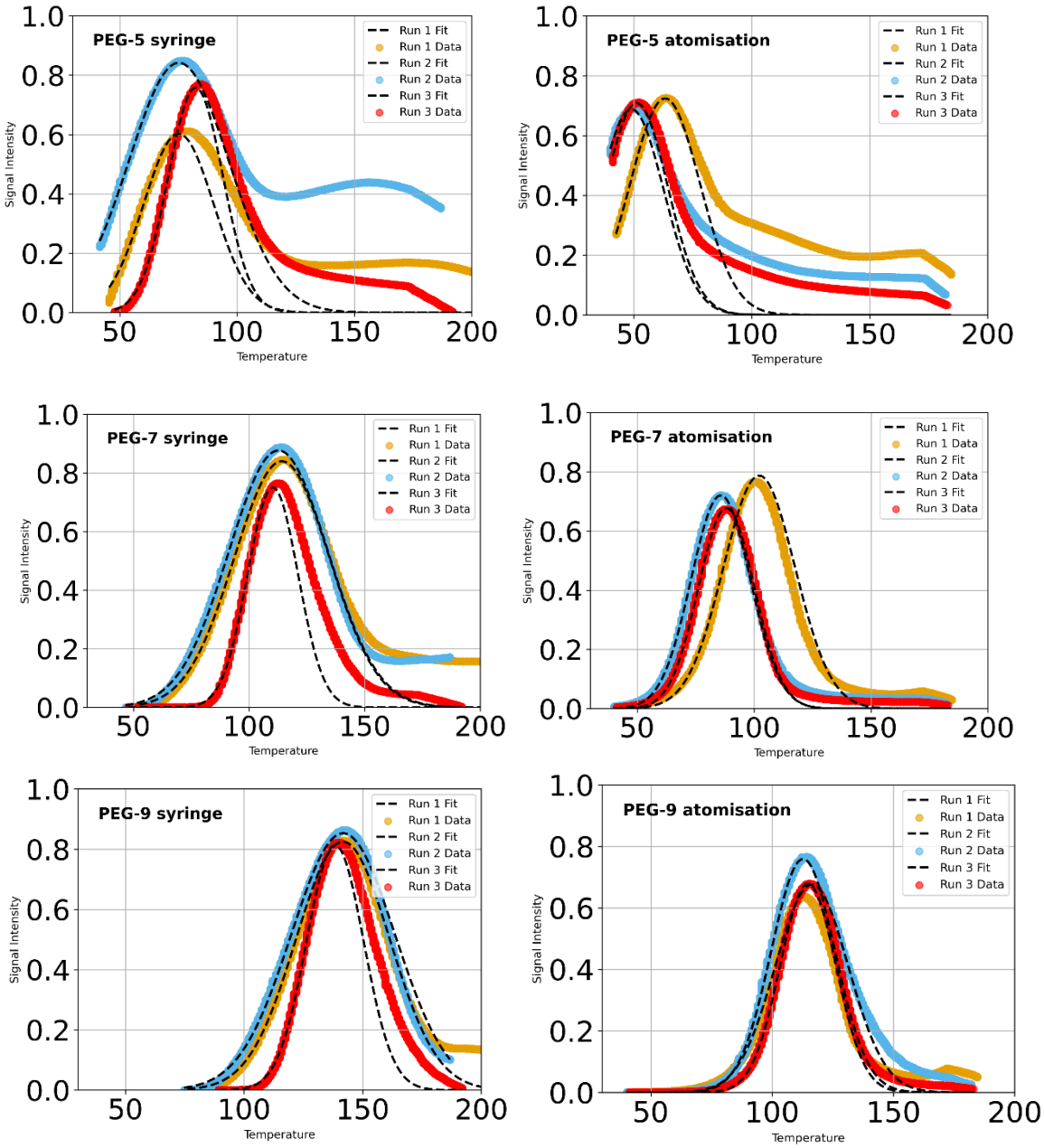
We thank the reviewer for their comment and agree that is trying to reflect the current state of the environment legislation. However, we would like to highlight that the phrase '*is no potential for atmospheric presence thus no further risk assessment in air is required'* refers to state of the EU legislation in which if a pesticide active ingredient is proven to be sufficiently involatile than no further atmospheric risk assessment is considered as the chance of volatilisation is negligible, thus the environmental and health risks due to atmospheric transport are low. Therefore we will adapt the manuscript to use the word negligible and clearly define that the phrases used are from the state of the legislation. Specifically the manuscript will be adapted to say the following 'as EU legislation *states that if a pesticide active ingredient is proven to be sufficiently involatile than no further atmospheric risk assessment is considered as the chance of volatilisation is negligible, thus the environmental and health risks due to atmospheric transport is low (Regulation (EC) No. 1107/2009'*

Line 283-286: In this discussion of thermogram shape and uniformity, some quantification of the PEG desorption curves may be valuable. What is their goodness of fit to a gaussian and their full width at half maximum?

We thank the reviewer for the comment and encouragement to delve deeper in to the statistics, these values are available be viewed in the supplementary material with the availability of the full width half maximum and standard deviation which has been added to earlier responses to the reviewer. In addition, a gaussian fit was produced for each of the thermograms and has been provided in the supplementary figures of the manuscript (S1). This was produced through mirroring the calculated gaussian (which was calculated using the Tmax, full width half maximum and standard deviations). The idea is the deviation from gaussian can give information on how the tail impacts the plot.

The following has been added into the manuscript to support this information:

'This observation is backed up by the gaussian fitted peaks shown in S1 (and complimentary statistics in S2) here a gaussian fit performed in the low side of the curve and mirrored (using the Tmax as the mirror line), assessing the gaussian shape of the thermogram which shows how the plot deviates from gaussian after the Tmax and therefore is not impacted by the tail before the Tmax.'



S1: Repeat run fitted with a low T-side gaussian fit with a mirrored high T-side fit from the PEG syringe thermograms presented in figure 6 of the main manuscript.

Figure 3a: Comparison between Ylisirnio et al (2021) using both methods here shows the increased Tmax associated with the syringe method over the atomization method which is well discussed here. However, Tmax data seems to be more consistent between the syringe method in both studies, with a bigger gap in Tmax observed between Ylisirnio and this study when atomization is used. Given that repeatability of vapor pressure measurements and consistency across measurement types is so poor, could you further explain/discuss if this apparent consistency when using the syringe method is desirable for vapor pressure estimation in targeted measurements?

The PEG calibration links the Tmax to the known vapour pressure of the PEGs. However, the process by which the FIGAERO is heated means that the evaporation rates of compounds from the filter surface will vary depending on the size of the liquid drop on the filter. A single large drop applied by

a syringe will take longer to evaporate at a given temperature compared to many smaller drops containing the same mass. Hence the calibration material needs to be applied to the FIGAERO surface in the same way as that of the analyte. This results in the atomisation method being preferred, as discussed at the beginning of reviewer 1's comments which is supported by the thermogram repeats in the supplementary material. As we discuss in the paper, our aerosol distribution applied to the filter surface was larger than that used in Ylisirnio et al and so our Tmax values are larger than theirs and exact comparisons between FIGAERO systems is not possible without ensuring the calibration particle sizes introduced onto the FIGAERO are similar. The repeatability of the syringing method is larger since it is harder to accurately replicate the droplet size introduced onto the filter. On the other hand when considering the comparison of the atomisation method, different (larger) droplet size distribution have been used in this study compared to that of Ylisirnio et al and so our Tmax v volatility relationship is shifted relative to theirs (further towards the syringe data). This results in the two calibrations not being comparable. Each set of calibrations are representative for the particular experiments since the aerosol size distributions of the investigated particles, in our case pesticides, were similar to those of the PEG calibration particles (figure 4). As a result, we recommend that the calibration particles used to derive the Tmax v volatility relationship are as close as possible to those of the particles whose volatilities are to be determined, as did Ylisirnio et al.

This is the case in figure 4 for all pesticides used except for 2,4 D and this is discussed in the results section. We have modified the text to make these points more clearly by adding the following text: '*Given the approach is subject to operational uncertainty we follow the recommendation of (Ylisirniö et al., 2021) and use the aerosolization method to determine pesticide vapour pressures on the basis that the atomisation method has a more robust repeatability and is more similar to atmospheric sampling conditions'.*

Figure 3b: There are two more points represented in the syringe data set than in the atomization data set. Why are these measurements not represented in Figure 5 (where both methods begin showing data at PEG-5)?

The PEG calibration curve using the syringe method extends to PEGs 3 and 4 whereas that of the aerosol method ends at PEG5 due to the effects discussed in the previous point. The smaller sized particles of the aerosolised PEG drops evaporate more rapidly from the filter than the larger syringed drops. The most volatile PEGs evaporate so rapidly from the small aerosolised drops that a Tmax cannot be resolved even at the lost temperatures of the ramp whereas the slower evaporation time of the larger syringed droplets means a peak can be resolved for the more volatile components.. The following will be added to the manuscript to increase clarity. *'Here, the Tmax values from PEG3-8 are reported for the syringe method and PEG 5-8 for the atomisation method, consistent with the available literature values presented by Krieger et al . As Kreiger et al state, this range covers all atmospherically relevant compounds that partition between gas and particle phases. As a result, while we can demonstrate that our approach to determining the Tmax of PEGs with the aerosol method can extend to larger PEGs we are unable to obtain a vapour pressure curve for these low volatilities at this stage. This analysis also demonstrates that since our thermograms closely resemble Gaussian distributions for PEGs 4 to 9 our results are representative across the whole range of relevant vapour pressures. Furthermore, vapour pressure values are only possible when injecting with the syringe due to the inability of the FIGAERO to measure the smaller more volatile droplets of PEG3 and 4 in the atomisation method due to rapid evaporation of the smaller droplets. Whilst beyond PEG8 the droplets are involatile and thus not atmospherically relevant*.'

Line 313-314: What differences are there between the size distributions used in this study and Ylisirnio et al (2021)?

The mode diameter of the PEG values reported in (Ylisirniö et al., 2021) are 60nm whilst the modal diameter of the PEGs in this study were 105nm. This statement will be addressed further in the reviewer's next comment.

Line 320-321 and Figure 4: Please provide some additional quantitative discussion of the particle size distributions observed (mode, total mass, spread, etc.) and if they are sufficiently similar to the PEG distribution for comparison and calibration per Ylisirnio et al (2021) as mentioned.

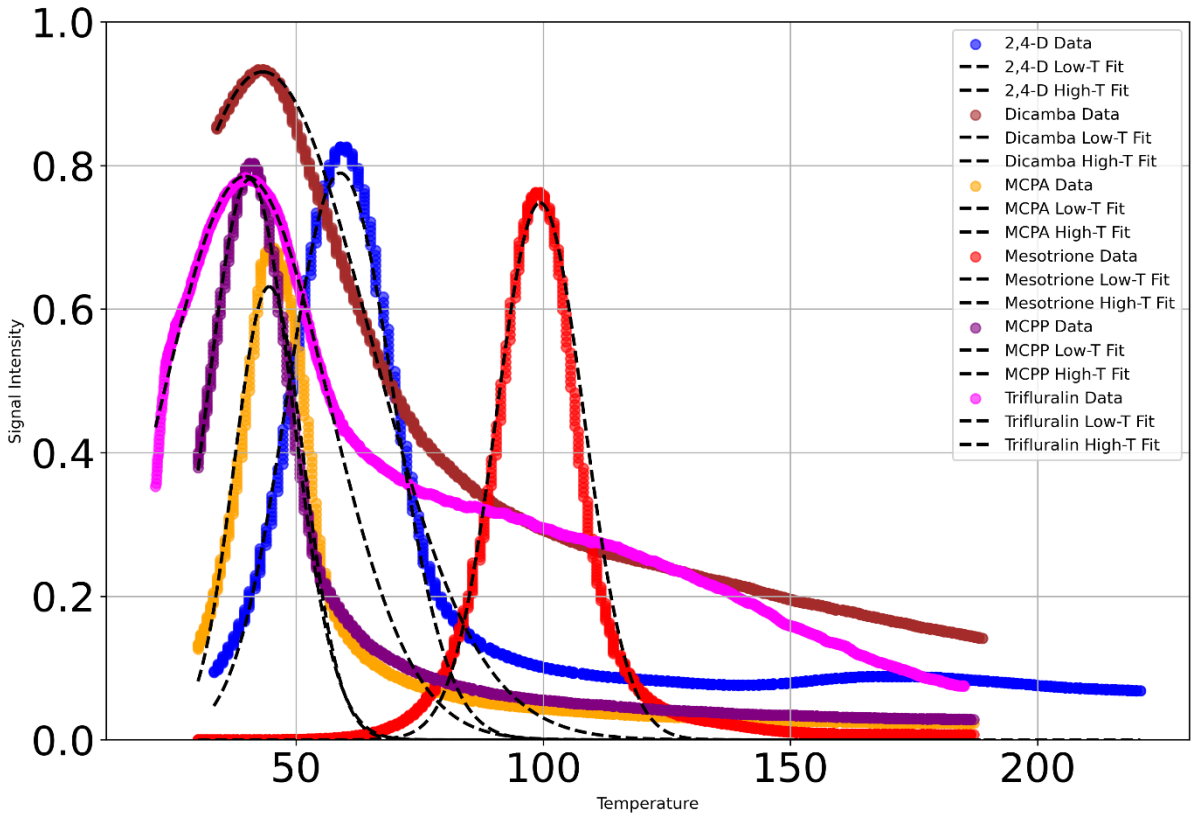
The referee is correct, this is the crux of many of the points raised in the discussion, which we hope we have clarified. The particle size distribution reported in (Ylisirniö et al., 2021) has a mode distribution value of 60nm. We have included a statement in this section to make this point more clearly: '*This is explained by the larger particle sizes used in the nebulisation of the calibration particles in this work (mode diameter~105 nm) compared to the previous work which had a smaller modal diameter of 60 nm. It is therefore not possible to directly compare the calibration curves but since the particles under investigation in both studies are similar in size to the calibration particles both calibrations can be effectively applied to the relevant experiments/. It is important to recreate the size distribution within the same investigation'.*

Figure 4: What density is assumed when calculated particle mass from SMPS particle volume distributions?

The density is assumed as 1000 Kgm^{-3} thus assuming uniform standard density.

Figure 6: The shape of the pesticide desorption peaks seems, at least by eye, much sharper than the PEG desorption peaks. Can you provide quantitative information about peak shape statistics? How closely do the pesticides follow a Gaussian desorption curve?

A table has been provided below and will be included in the supplementary of a revised paper that includes the full width half maximum and standard deviation of each of the thermograms presented in this study. This suggests that the FWH maximum of the pesticides is predominately lower than in the PEGs. Additionally, we are able to compare the gaussian fits of the PEG calibration (shown in an earlier comment) with the pesticide gaussian fits shown below. Here it can be seen that all of the pesticides fit the gaussian peak well and that any deviation from gaussian occurs after the Tmax and therefore is not impacted by the tail before the Tmax.



S3: Gaussian fitted pesticide thermograms presented in figure 6 of the main manuscript.

Figure 6 and Figure 7 and associated trifluralin discussion and conclusions: The thermogram shape of trifluralin in particular is unique and worth discussion. It sharply appears at near 30 degrees and then peaks with a long tail to the right. Is this evidence of excessive trifluralin loading? Some type of thermal decomposition product? Furthermore, the Tmax for trifluralin in Figure 7 does not look correct based on Figure 6. There, the Tmax appears closer to 45 or 50 C, not the 27.7C reported. Please assess and correct as needed.

The Tmax of Trifluralin was replotted and the correct x axis temperature was used, and thus the 27.7°C is the correct value. This has been addressed in a previous point.

Line 363-365: This brief discussion of the potential bias in vapor pressure measurement of 2,4-D here is useful. Is there any method for extending this potential bias quantitatively to capture the anticipated error or uncertainty in the FIGAERO-CIMS volatility measurement?

We agree with the referee that the discussion of potential bias of 2,4-D is useful because the size distribution is shifted to smaller sizes compared to the other experiments and the PEG calibration particles. The peak in distributions of the PEGs and most of the pesticides is 105 nm whereas that of 2,4 D is around 90 nm, 15 nm less. The Ylisirnio calibration used a distribution of particles with a peak at 60 nm and shows approximately the same Tmax for PEG6 as we show for PEG5 (see figure 3). In fig 3b a 15°C shift (a shift in PEG6 to PEG5) leads to a 3 orders of magnitude change in volatility. Since we see a 15 nm size shift for 2,4D compared to a 45 nm shift between the value presented here and Ylisirnio. For small droplets of a few microns in diameter evaporation is close to the kinetic regime, in which the droplet diameter decreases linearly with time (Vlasov, 2021). This results in approximately one of magnitude difference in volatility. This is broadly consistent with Fig

8. A more thorough investigation of these effects is beyond the scope of this work and more detailed calibration work, most likely on monosized aerosol would be needed to quantify these effects.

Line 396 "This does not impact the FIGAERO-CIMS measurements which relies on thermal decomposition.": What is meant here? FIGAERO-CIMS measurements rely on thermal desorption and thermal decomposition can and does occur in the FIGAERO, leading to multimodal thermograms which require additional processing to appropriately separate desorption and decomposition.

Our apologies for the confusion and thanks to the referee. The FIGAERO does not rely on thermal decomposition, rather on thermal desorption. However, the referee is correct that decomposition can and does occur in the FIGAERO. The following has been added to the revised version of the manuscript *'However, Mesotrione can still be considered to be involatile as if a pesticide at the higher temperature (100°C) is non-volatile it will not be more volatile at 25°C and thus extrapolation to a lower temperature is not required'*

Line 478-479, "Unfortunately, the reports do not specify which particular method was utilized. Consequently, it cannot be assumed that the pesticide literature values can be completely reliably compared due to the substantial variations in these methods.": Can the potential variation in methods be displayed for example in Figure 8 to capture the potential spread of literature values compared to the measurement conducted here? Are there other literature sources to display in Figure 8?

We thank the reviewer for this point. The value is based on the regulatory framework and is not readily traceable. It is based on an upper limit value made at a higher temperature and is included for reference. We will include the sentence above to clarify this point in the revised paper. The authors recognise the importance of the suggestion of highlighting the different methods used in figure 8 in which the literature value is an upper limit made at higher temperature that is included for reference and thus shows a limitation in the results. However, a separate discussion may be suitable to understand the requirements of providing more openly available data and methods within industry, this is beyond the scope of this manuscript.

Line 496-498, "Despite this a study in Arctic monitoring stations found low levels of Trifluralin in arctic air(Balmer et al., 2019) and has now been predicted that small amount of Trifluralin may stick to aerosol particles and transported significant distances.": This is inconsistent with your current observation of Trifluralin as an IVOC which would partition sparingly to aerosol particles. As per a comment above, please confirm that your data agrees with the Tmax and volatility characterization presented here. If it does, please discuss relevant literature and mechanisms that may allow Trifluralin to be transported to the Arctic even with a short atmospheric oxidation lifetime and high volatility.

We thank the reviewer for their comment and understand the possible confusion of this statement. In the discussions re Trifluralin's withdrawal from use in the EU (Efsa, 2009) one of the discussions brought forward was this comment in which Trifluralin is expected to be volatile with a short oxidation lifetime and thus would not expect to be observed in the Arctic air, however despite this it has been measured at Arctic measurement stations suggesting an un-confirmed mechanism of transport is present. The authors appreciate that there may not be enough literature to support the comment highlighted by the reviewer and thus the following amendments have been made to the manuscript:

'Studies in Arctic monitoring stations have reported low levels of Trifluralin in arctic air (Balmer et al., 2019). At present the mechanism giving rise to such long range transport are not clear, however the finding of trifluralin in such a remote environment was a major contributing factor to the removal of Trifluralin's approved status for use in the EU (Efsa, 2009).'

Technical Corrections

Line 122: “maybe” to “may be”

This has been corrected.

Figure 2: Presenting these thermograms with the same horizontal axis in both panels will make the Tmax shifts more clear.

This has been corrected.

Figure 3: Increased marker size and consistency in marker choice for delivery method from this study across both panels would improve legibility. In 3b, I would suggest using log(vapor pressure) not ln(vapor pressure) for greater consistency across figures and more straightforward comparison to text values.

Marker choice has been made consistent. Ln is used instead to keep the axis consistent to equation 2 in which the equation of the lines represents equation 2.

Figure 4: Units on vertical axis.

We thank the reviewer for their comment. The vertical axis plots the dM/dlogdp from an SMPS measurement with the units of $\mu g/cm^3$, this has been amended.

Figure 7: Where error bars appear in a figure, what they represent should be listed in the figure caption. Vertical axis label should use a subscript for “max”

This has been corrected.

Figure 8: Increased marker size may be useful for legibility. In addition, error bars where possible should be included. Panels could be oriented side by side and use a shared legend. Finally, are multiple literature sources used in this figure? In that case, each literature source should have its own symbol and be clearly cited. If only one source is used, that should be listed in the legend and cited in the caption.

This has been corrected. Additionally, a label of a and b has been added to the figure for clarity.

Figure 9: This figure is extremely difficult to read, though this may be due to some upload issues. In any case, I would suggest that the labels for the points not be cut off by the frame, and use of a legend might be more appropriate anyway. I would also suggest using log(Vapor Pressure) rather than ln(vapor pressure) to make the values in the text more easily read off of the chart and for consistency with earlier figures on a log scale. Finally, labels such as “stated literature value” are not useful. Indicate which specific literature source is used for that point, I believe this would be the University of Hertfordshire Pesticide Properties Database.

We thank the reviewer for the comments and the necessary amendments have been made.

Table 2: Reported values should include uncertainties (standard deviation or similar).

Balmer, J. E., Morris, A. D., Hung, H., Jantunen, L., Vorkamp, K., Rigét, F., Evans, M., Houde, M., and Muir, D. C. G.: Levels and trends of current-use pesticides (CUPs) in the arctic: An updated review, 2010–2018, Emerging Contaminants, 5, 70-88, 10.1016/j.emcon.2019.02.002, 2019.
Bannan, T. J., Le Breton, M., Priestley, M., Worrall, S. D., Bacak, A., Marsden, N. A., Mehra, A., Hammes, J., Hallquist, M., Alfarra, M. R., Krieger, U. K., Reid, J. P., Jayne, J., Robinson, W., Mcfiggans, G., Coe, H., Percival, C. J., and Topping, D.: A method for extracting calibrated volatility information from the FIGAERO-HR-ToF-CIMS and its experimental application, Atmospheric Measurement Techniques, 12, 1429-1439, 10.5194/amt-12-1429-2019, 2019.
Bilde, M., Barsanti, K., Booth, M., Cappa, C. D., Donahue, N. M., Emanuelsson, E. U., Mcfiggans, G., Krieger, U. K., Marcolli, C., Topping, D., Ziemann, P., Barley, M., Clegg, S., Dennis-Smither, B., Hallquist, M., Hallquist, Å. M., Khlystov, A., Kulmala, M., Mogensen, D., Percival, C. J., Pope, F., Reid, J. P., Ribeiro Da Silva, M. A. V., Rosenoern, T., Salo, K., Soonsin, V. P., Yli-Juuti, T., Prisle, N. L., Pagels, J., Rarey, J., Zardini, A. A., and Riipinen, I.: Saturation Vapor Pressures and Transition Enthalpies of Low-Volatility Organic Molecules of Atmospheric Relevance: From Dicarboxylic Acids to Complex Mixtures, Chemical Reviews, 115, 4115-4156, 10.1021/cr5005502, 2015.
EFSA: Conclusion on pesticide peer review regarding the risk assessment of the active substance trifluralin, EFSA Journal, 7, 327r, 10.2903/j.efsa.2009.327r, 2009.
Krieger, U. K., Siegrist, F., Marcolli, C., Emanuelsson, E. U., Gøbel, F. M., Bilde, M., Marsh, A., Reid, J. P., Huisman, A. J., Riipinen, I., Hyttinen, N., Myllys, N., Kurtén, T., Bannan, T., Percival, C. J., and Topping, D.: A reference data set for validating vapor pressure measurement techniques: homologous series of polyethylene glycols, Atmospheric Measurement Techniques, 11, 49-63, 10.5194/amt-11-49-2018, 2018.
Vlasov, V. A.: On a theory of mass transfer during the evaporation of a spherical droplet, International journal of heat and mass transfer., 178, 121597, 10.1016/j.ijheatmasstransfer.2021.121597, 2021.
Ylisirniö, A., Barreira, L. M. F., Pullinen, I., Buchholz, A., Jayne, J., Krechmer, J. E., Worsnop, D. R., Virtanen, A., and Schobesberger, S.: On the calibration of FIGAERO-ToF-CIMS: importance and impact of calibrant delivery for the particle-phase calibration, Atmospheric Measurement Techniques, 14, 355-367, 10.5194/amt-14-355-2021, 2021.