Responses to reviewer's #2 comments

Jackson et al, present vapour pressures for six pesticides measured using the FIGAERO-ToF-CIMS analytical technique. There is a large discussion around the method of delivery of the pesticides onto the filter contrasting direct injection and atomisation. The method of calibration against a series of PEG compounds with known vapour pressures is also presented. The measured values are also contrasted with literature values and two SAR models.

This manuscript is of excellent scientific significance as it demonstrates the utility of the FIGAERO-ToF-CIMS measurement technique for investigating the volatility of -pesticides with high environmental relevance. This manuscript should be considered for publication after considering several major and minor comments.

We'd like to thank Referee 2 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). A marked-up version of the manuscript detailing the amendments from all of the reviewers comments is also provided.

Major comments

The manuscript is extremely comprehensive regarding background, summarising the current state of knowledge and where these new finding fit in a literature and regulatory context.

While informative, large parts of the text are quite verbose and do not seem entirely relevant to the focus of the manuscript. Additionally, throughout the manuscript and specifically in section 4.1, there seems to be a lot of repetition. In some instances, the text does not match the section it is found in, for example there is some description of the experimental method at the end of the SAR section. I found the discussion on comparisons with the literature quite hard to follow, mainly due to the lack of clarity around which 'literature' is used for comparisons.

That being said, these issues concern the presentation of the study, rather than the study itself. I think the manuscript would benefit greatly from editing down to focus on the key message(s) and better connecting the bigger picture issues of regulation and reporting to the results. More efficient organisation of the text would also greatly improve its focus. This would also give the author the opportunity to check some grammar issues and typos.

We thank Referee 2 for the major comment stated regarding the background information. This was also picked up in referee 3's comments. We are encouraged that the referee is positive about the thorough introduction and literature study being important, but we note that they request sharpening the text and reducing the verbosity. We will endeavour to retain the essence of the discussion in a revised version whilst sharpening the text and reducing it in size.

Minor comments

Line 87 – "effectively shielded from degradative gas phase oxidation". It would be nice to contrast this with condensed phase chemical processes. Is it possible to say something about the lifetime of the pesticide in the gas vs the condensed phase?

We thank the reviewer for pointing this out. Line 87 refers specifically to the pesticide difenoconazole which has been found to reside predominantly in the particle phase due to its vapour pressure of 3×10^{-8} Pa, making it rather involatile in the atmosphere and thus would not be expected to reside in the gas phase for any significant timeframe.

However, with respect to the pesticides in this study estimations of condensed phase reactivity are relatively unknown due to the lack of understanding of many pesticides in the atmosphere environment (Brüggemann et al., 2024) and thus a more extensive experiment would be required to be undertaken, beyond the scope of the manuscript. With this the following has been added to the updated manuscript '*the very low vapour pressure of difenoconazole is making it practically involatile and thereby unable to react in the gas phase'*

Line 93 – what is meant by "activated process"?

We thank the reviewer for pointing this out. In our editing down and refocusing of the introduction this phrase has been removed from future versions of the manuscript.

Line 95 – what is meant by "pesticide active substance"?

We thank the reviewer for pointing this out. The pesticide active substance refers the active ingredient in the pesticide formulation i.e. the compound with the pesticidal properties. This is defined in line 40. To improve clarity the definition in line 40 has been edited to refer to definition as defining both pesticide active ingredients and pesticide active substances.

Line 125 (167) – what is meant by "reverse flushed"?

We thank the reviewer for highlighting this. This comment was also addressed by reviewer 1. 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, the line now reads '*The filter (and any particles on it) is flushed with nitrogen and continuously heated at a rate of 8.75°C min^{-1}.*' This has been updated for further versions of the manuscript.

Line 146 – what "coefficient" is gamma?

We thank the reviewer for highlighting this. The sentence should have read γ = condensed phase activity coefficient, which for pesticides is assumed to be 1. This has been updated for future versions of the manuscript.

Line 182 – flow of 20 Lm-1 of what gas?

We thank the reviewer for highlighting this. The gas referred to is purified compressed -air connected to a mass flow controller to control the flow of 20Lmin^{-1}. This has been edited into the manuscript.

Line 187 – Through -> although

We thank the reviewer for pointing this out. This has been corrected in the revised manuscript.

Line 199 - I found the description of SAR a little confusing and not introduced particularly clearly. For example, section 2.2 misses directly stating that SAR is used to predict vapor pressures, and there is no explanation of why the Nannoolal and MGM models are chosen specifically. I think this can be easily corrected by reformulating the text.

We thank the reviewer for pointing this out. This has been corrected in the revised manuscript to say the following '*Structure activity relationship models are commonly used as a first prediction and screening tool for a compound's physiochemical properties (including vapour pressure) and thus environmental fate and behaviour'*

Additionally, the clarity of the SAR method section has been adapted to reflect the reasoning behind the uses of the different vapour pressure estimation methods to say the following: '*The Nannoolal model was chosen because the vapour pressure observations used as training data for the*

development of the model included a large number of aromatic compounds, with a wide range of functional groups'

Line 200 – estimation methods of what?

This refers to the estimations of- physiochemical properties, specifically vapour pressure in this study.. We thank the reviewer for pointing this out and the manuscript has been revised: '*Estimation methods are required to predict the vapour pressure of atmospherically relevant compounds and are commonly achieved through equation-based estimation methods'*

Line 208 – "The Nannoolal model was chosen as training data for the model" doesn't really make sense.

We thank the reviewer for the comment, the new versions of the manuscript have been reworded to more clearly state the following – '*The Nannoolal model was chosen because, the vapour pressure observations used as training data for the development of the model included a large number of aromatic compounds, with a wide range of functional groups'*.

Line 263 – what is a PPP?

We thank the reviewer for the comment, PPP is plant protection product, this is defined in line 39 of the original manuscript.

Line 283 – the commercial PEG solution is a great benefit. Can you explain a bit more about why you are using PEG-4 as your lower Tmax limit? Although the atomisation method is only useful down to PEG-5, it doesn't look like the syringe method is great below that either? There is actually some discussion of this at line 338.

We thank the reviewer for this comment, a similar comment was raised by reviewer 1, the response to reviewer 1 a summary of the response is shown below:

Commented [HC1]: Copy alterations/suggestions in here

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. In terms of the experiments carried out in this manuscript, the smaller sizes of the aerosolised PEG drops on the filter evaporate more rapidly at lower temperatures and hence cannot be measured by the FIGAERO method, whereas the larger syringed drops of the most volatile material remain present until larger Tmax values. The following has been 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. The discrepancy between the two methods is due to the inability of the FIGAERO to measure the smaller more volatile droplets of PEG3 and 4 in the atomisation method'.*

Line 289 – I wonder if a 1:1 plot of atomisation vs syringe Tmax values for each PEG would give any insights into the systematic bias of the syringe technique?

We thank the reviewer for this comment, a detailed response to this issue has been provided in reviewer 1.

Line 304 – is it possible to say more about the impact of the 0.1 g/L vs 0.5 g/L deposition on the filter on the Tmax?

We thank the reviewer for the comment. We would like to direct the reviewer to the publication referenced in the text (A. Ylinsirniö et. al. 2021), which explores the differences between concentrations of particles on the filter. To add clarity, the following was added to the manuscript: '*It was suggested that an increase in concentration on the filter leads to higher Tmax values due to more energy required to evaporate off the filter. For the atomisation method, equation 3 was introduced to*

monitor the time required for the required mass to be deposited on the filter. This varies due to the output of the atomiser and is measured using the SMPS-CPC. Here, the integrated mass over the duration of the sampling period provided the total mass collected. '

Commented [OJ2]: Add text to manusxript

Line 315 – "small but consistent repeatable effect". This isn't explained well here but I think this explained more fully on page 17 later. This is a good example of repeated information in two different places. It would be good to summarise this information in one place – maybe you can make a comment on the variability of particle diameter and how it affects Tmax in this instance – is it possible to have a metric like x degrees C / nm? Is the variation here significant?

We thank the reviewer for the comment and in the updated manuscript we have aimed to keep the information clear. The small but consistent repeatable effect refers to the effect due to the differing size to volume ratios of different sized particles found by (Ylisirniö et al., 2021). However, this exact value should not be used for the experiments presented here as different FIGAERO-CIMS should not be compared against when considering exact values. Despite this the change in Tmax of 7°C between particle sizes of 80 and 300nm determined in the previous publication can be considered as significant as it may lead to differing vapour pressures, to mitigate this, as suggested in this manuscript particle sizes must be kept the same in the same investigation.

A similar comment was made by reviewer 1, in which a more in-depth explanation is provided. We have included a statement in this section to make this point more clearly: '*This is explained by the increase in particle sizes used in the nebulisation of the calibration particles in this work compared to the previous work which had a smaller modal diameter of 60 nm (compared to the 105nm in this study). However, it must also be noted that it would be inappropriate to compare the exact measurements between the two non-calibrated FIGAERO set ups, instead it is important to recreate the size distribution within the same investigation*'.

Commented [HC3]: This answer needs to be much more brief and also add clarity. The general reader nor the editor will have any understanding of either the comment or your answer. I suggest Typing out the original sentence to give context and give a brief specific answer and refer to ref 1 answers more generally

Line 357 – "... highest tmax was for the least volatile pesticide .." least volatile according to who? Are you referencing a literature value or the fact that the tmax is highest for mesotrione?

We thank the reviewer for the comment, By definition the compound with the lowest Tmax will be the most volatile according to numerous sources including the Tmax values calculated by the FIGAERO as shown by the calibration curve in figure 3b and calculated by equation 2. To make this clearer, we added in the main text 'The raw thermograms (fig. 6) and eq. 2 were used to calculate the T_{max} values presented in figure 7, where the highest T_{max} was for the least volatile pesticide…"

Commented [AV4]: As I mentioned in the comment above, I think you can provide some more direct answers to the reviewer's queries. It will make a lot easier the review for them and less likely to get pissed off that you dodged the question or not properly replied.

Commented [OJ5]: Finish and add to text

Line 364 – Figure 8. These need an (a) and (b). Which Literature Value is being referred to in the legend? It would be better if the legend handle was a bit more descriptive.

We thank the reviewer for pointing this out. This has been corrected in future versions of the manuscript.

Line 376 – what is a "regulatory endpoint value"?

The "regulatory endpoint value" refers to the 'endpoints' defined in line 112 of the original manuscript in which the regulatory body it is referring to is EFSA (European Food Safety Authority).

Line 382 – MGM vs MGM SAR these refer to the same thing but are given different names.

Thank you for pointing out a possible confusion the SAR refers the MGM in being a Structure activity relationship model as defined in section 2.2 of the methods and thus is two acronyms, both previously defined in the text. To avoid any further confusion the 'SAR' has been removed from the phrase in future versions of the manuscript.

Line 385 – what is meant by comparison data? It would be better to be more specific with the literature value you are comparing to.

We thank the reviewer for the comment. The 'comparison data' refers to all the measured and modelled values compared for the Mesotrione pesticide in figure 8a. To avoid confusion, the future version of the manuscript has been changed so that the phrase reads: Mesotrione exhibits the greatest discrepancy between the measured values and the modelled values'

Line 386 – The University of Hertfordshire Pesticides Properties Database for Mesostrione is mentioned here, and then two lines later, the EFSA endpoints, from which the database draws its data. This section reads very narratively which is confusing, i.e., I am not sure it is necessary to explain that the database had a suspect value but on further inspection it was because the underlying EFSA data is measured at a different temperature. This just highlights an issue with the database.

It might be easier to standardise the way you refer to the different literature data earlier on to make this easier to follow. Is the "upper limit" value the green "stated literature" value in figure 9? Using these different terms is hard to follow.

We thank the reviewer for the comment and apologise for the confusions. In addition to other reviewers comments we have improved the clarity of this paragraph. It now reads:

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 since lower vapour pressures will occur at lower temperatures. We calculate the vapour pressure at 293K based on earlier work at higher temperatures (Efsa, 2016) 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.

The observations at ambient temperatures presented in this work show Mesotrione to be considerably less volatile than may be expected based on the upper limit value, . It can be seen that the reason for the difference in the EFSA document (Efsa, 2016) is that the method used observed some thermal decomposition of Mesotrione (the melting point temperature is stated to be ~165°C/438K "with some decomposition on melting). However, Mesotrione can still be concluded as 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.

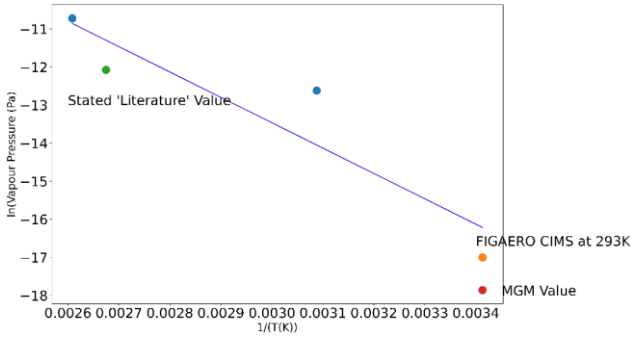
Commented [HC6]: Ensure this includes my suggested changes to ref 1 response.

Line 394 – I am not entirely sure why thermal decomposition is mentioned here. What does difference in the EFSA document mean?

We thank the reviewer for the comment. the literature lacks detail on the reasons for this and so this sentence will be removed in the revised version of the manuscript.

Line 405 – Figure 9. What are the different "literature measurements at varying temperatures"? where do they come from? It would be more informative to have the sources rather than stating they are measured at various temperatures (this is what the x axis shows already). The 'stated literature value' is just plotted at the wrong 1/T value. If measured at 373K then this should be plotted at 1/373 = 0.000268 and so would appear to follow the trend.

We thank the reviewer for this comment. The placing of the literature value was meant to highlight where the literature value would be placed on the Clausius Clapeyron graph if the stated literature value was taken at 20°C and not the 100°C it was actually determined at. However, we recognise this was confusing so the plot has been replotted (as shown below) to show the true temperature at which the literature value was determined, in agreement with this comment the point now aligns with the trend.



In addition, the following clarification has been adapted to the manuscript to further explain how figure 9 was plotted: '*Figure 9 plots each of the measured values (at 323K, 373K, 383K) taken from EFSA's list of endpoints and compares these values to the FIGAERO-CIMS measurement and the MGM predicted value.*' Additionally, the caption to figure 9 now states: ' *Figure 9 Clausius Clapeyron plot of Mesotrione measurements from the EFSA endpoint report (Efsa, 2016) determined at varied temperatures (323K, 373K, 383K). This is then -compared with the CIMS atomisation measurement and the Modified Grain Method (MGM). Points in blue are the values from the EFSA endpoints Efsa, 2016).*'

Line 418 – "within an order of magnitude". It is of course good the difference in values is less than an order of magnitude, but without uncertainty measurements it is difficult to assess how 'good' the agreement is. Either a measure of the variability or uncertainty.

We thank the reviewer for the comment. Figure 8a contains error bars for the CIMS measurements, this has been highlighted in the legend/caption of the figure. However, are small enough due to the high repeatability of the Tmax in these experiments. The following has been added to the figure 8 caption ' *The values come from the average of 3 runs shown in figure 7. The error bars are shown on the figure however are not visible due to the high repeatability.*' On the other hand, a comparison of the accuracy of each of the methods has not performed in previous studies and thus a full conclusion may be inappropriate. A study using a number of different compounds not just pesticides would be required to assess the performance. This is especially important when considering the comparisons with the models. This is beyond the scope of the manuscript.

Line 420 – Do you expect higher volatility with more functionalisation? Can you explain further?

We would like to thank the reviewer for the comment. On reconsideration of the trend we have consequently, replaced this sentence with the following, which gives a more meaningful and insightful interpretation of the estimation methods. *'Overall, both models may lead to misleading indications of the environmental fate of a pesticide. This is because the MGM, and to a lesser extent Nannoolal, predicts likely gas-phase presence of 2,4-D, dicamba, MCPA and MCPP, whereas measurement indicates a much stronger tendency to be present in the particle phase, or to remain on the target application*.'

Line 456 – "Lower volatility compounds are unlikely to be atmospherically relevant if applied to the surface in the liquid or solid phase". I take it this refers to application of pesticide to the surface of a plant? Low volatility compounds are of course atmospherically relevant in an aerosol context.

We thank the reviewer for the comment and agree that the message of the last sentence is confusing and may be irrelevant for this section. Of course, low volatility compounds are atmospherically important in the an aerosol context. However, from legislation perspective low volatility compounds present minor concern as they do not expect to be important for long-range transport. This has been picked up by another reviewer (see below) and we have made an effort to be clearer about the context of our statements. In the light of this, the authors have decided to remove the last two sentences to aid with clarity.

The following comment was also made by reviewer 1. A more in depth response and the detail of amendments can be found here.

Line 457 – I don't understand the message of the last sentence of this paragraph.

We thank the reviewer for the comment and agree that the message of the last sentence is confusing and may be irrelevant for this section. The authors have decided to remove the last two sentences to aid with clarity.

Line 467 - "training dataset" what data does this refer to? This is the Nannool training data? I think this just requires more consistency in naming.

We thank the reviewer for the comment. 'Training data' refers to training data sets used for both the MGM and Nanoolal models. This has been made clearer for future manuscript versions and reads '*…the chlorinated benzene or carboxylic acid function groups may have been poorly represented in the training data set used to develop the MGM and Nannoolal models'*

Line 470 – "fishtine factor" needs introducing earlier in the text.

We thank the reviewer for the comment, The fishtine factor refers to the factor used in the calculation of the model, however on further review the authors believe that is inappropriate to include in the context of the Nannoolal model. Instead, a general comment was added to allow further comparison. This was: 'For four of the five pesticides where both estimation methods were applied, the Nannoolal method gave better agreement with observed vapour pressures, consistent with the findings of Barley and McFiggans (2010) (which included multi-functional aromatics).'

Line 490 – " … volatilisation is a major degradation mechanism .. " volatilisation doesn't degrade the active ingredient, I guess this means degradation of the pesticide product itself?

We thank the reviewer for the comment, the manuscript has been altered to be correctly phrased: '…volatilisation is a major mechanism of loss from the initial application site.'

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