Responses to reviewer’s #3 comments

This study examined the volatility of pesticides using a novel approach, the Filter Inlet for Gases and AEROsols (FIGAERO) coupled with a chemical ionization mass spectrometer. Two compound delivery methods were tested, and the results were compared with those from previous studies. Volatility values were also evaluated against literature data, with potential explanations provided for discrepancies between measured and reported values. The atmospheric implications of pesticide volatilities are further discussed.

The scientific method used in this study is sound, and the results are meaningful and show promise. Additionally, the topic is significant and relevant to the field. However, I believe this manuscript is still in the draft stage and requires improvement in several key areas before it can be considered for acceptance. Overall, I would recommend rejecting the manuscript in its current form.

We’d like to thank Referee 3 for their 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:

Many sentences in the manuscript are either grammatically incorrect or lead to confusion, making it difficult for readers to understand the content easily. For example, I’ve noted several specific instances, but I believe there are many others throughout the paper that require improvement. I recommend reviewing the entire manuscript to enhance clarity and readability.

Thanks to the reviewer for urging us to improve the clarity of the paper. This has been thoroughly considered as presented in the revised version.

Line 18-19: I feel it would be better if the sentence can be revised as “ The pesticide volatilities were compared with widely accepted standard literature values used in industry, as well as values derived from a common environmental model frequently employed in industrial applications.

This sentence was improved for clarity and brevity according to the reviewer’s comment.

Line 32-33: It may be better like this “Pesticides are a group of compounds whose fate and behaviour in the atmosphere are less studied and characterized compared to their behaviour in soil, surface water, and groundwater environments.” The original sentence creates confusion by comparing the "environment" (which includes soil, surface water, and groundwater) with specific parts of the environment.

This sentence was improved for clarity by removing references to the environment. The sentence now reads the following in the amended manuscript: ‘*Pesticides are a group of compounds whose fate and behaviour in the atmosphere is less well studied and characterised in comparison to soil, surface water and ground water environments’*

Line 1-83: This is verbose and needs to be more concise.

We thank the reviewer for this comments. This has also been picked up by reviewer 2.We have sharpened up and reduced the verbosity of this text as presented in the marked-up version of the manuscript. We endeavour to retain the essence of the discussion in a revised version whilst sharpening the text and reducing it in size.

Line 97-106: Instead, it would be helpful to provide a more detailed introduction to the various methods used for vapor pressure measurement, as readers may be particularly interested in this aspect.

A similar comment was made by reviewer 1. A detailed response has been provided in the response to reviewer 1.

Figures: Figures are not well presented in this manuscript.

We thank the reviewer for the comment. The following has been considered in the new version of the manuscript to improve the clarity, presentation and consistency of the figures in the manuscript. Specific notes that have been improved include the consistency of brackets in the axis units of figures, the consistency of the size of the text and figures and superscript of units.

2. The workload of this study may not be sufficient for an *ACP* paper. I recommend expanding the scope by measuring more pesticides. For example, in Figure 6, we see that the Tmax for most compounds falls between 25-50°C.

We disagree strongly with this comment. The work shows how the FIGAERO-CIMS method can be applied to an important class of compounds whose vapour pressures are important in both industry and environmental science yet are very poorly defined. Previous methodologies all have some shortcomings and so a new approach is a valuable addition to the available literature. To make this more obvious the following has been added to the introduction: '*The object of this work has not been to deliver a wide-ranging study of the vapour pressures of many pesticides but rather to select a number of important pesticides based on clear criteria to demonstrate the experimental approach is a robust one and to compare with currently available literature'*. We hope that we have demonstrated the utility of the method and so future work may generate vapour pressure data for a wider set of pesticide compounds. Each of these observations is a substantial amount of work so we made sure that we selected our compounds on the following characteristics: the compounds are or have been widely used; they represent different types of pesticide classes; they have different chemical functionalities; and they also have been previously observed in the environment remote from application implying an atmospheric transport pathway. This is described clearly in section 2.4. Both other reviewers are strongly supportive of this approach. Reviewer 1 notes that *"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 environmen*t." And reviewer 2 states that "*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.*".

Additionally, we would like to make the referee aware that pesticides are a group of compounds with specific functionality and thus commonly would be expected to have a Tmax within 25-50°C. The authors would also like to point the reviewer to the main theme of the manuscript which refers to atmospherically relevant compounds. The authors feel as though that choosing pesticides of a wider range of Tmax/vapour pressures would misrepresent pesticide active ingredients and go beyond the focus of this work.

There are also several alternative approaches the authors could take to make the paper more impactful and insightful:

- **Conduct additional experiments** if the current data is not ideal. For instance, with 2,4-D, if the one-order-of-magnitude difference is thought to be due to smaller particles, why not attempt to make the particle sizes more consistent with other measurements to confirm this assumption?

  Using the nebuliser and solvents that were available to us we were unable to generate a particle size distribution for 2,4D that matched the size distribution of the calibration PEG compounds. Nevertheless we felt it important to include these results in the paper rather than removing them to show the size of the potential bias in the results if the size distributions do not agree. It further supports the discussions around aerosolization and the using appropriate drop sizes in both the calibration and observation. We have explicitly stated the shortcoming of our results for this compound and discussed potential reasons why there may be a high bias in our result. Unfortunately, we are unable to return to this work within a reasonable timeframe and so either need to remove the 2,4D results from the paper or include them with a discussion over the differences with previous literature. We have chosen the latter as we feel this adds information for the reader and future user of the work, cautioning that it is important to generate the correct size drops.

- **Dive deeper into the experimental results.** In Figure 2, why do the calibration curves for the syringe method show a more Gaussian distribution compared to the atomization method? In Figure 3b, why is linear fitting done using only a few points from Figure 3a? What are the R^2 values for those two fits? While I understand that the syringe method might shift Tmax due to droplet effects, does this mean the syringe method cannot provide a better linear relationship? As discussed in the paper, particle size also influences the derived vapor pressure. We really need to show more details of the experimental results before making a conclusion.

We thank the reviewer in the encouragement of some of these comments have been specifically addressed in reviewer 1 and 2's comments. However, for clarity it will be explored further here. Firstly, to support this repeated measurements we have amended the manuscript to further delve into the experimental results, this has included providing repeats of thermograms of all the experiments presented are provided in the supplementary 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.

Additionally, the authors would like to clarify the argument presented in this paper regarding the syringe and atomisation method. Firstly, 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. 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. Additionally, it has been previously observed that the size of the aerosol 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. 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 repeated runs provided in the supplementary), due to the spread of energies required to evaporate the compound being broader. Overall, this effect means we propose the atomisation method is more suitable. In the amendments throughout the paper, we hope the reviewer is able to further appreciate the requirement for this calibration . Consequently, due to the above arguments it must be considered that when comparing data. 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.

In addition, the reason for the fitting in 3b only using a few of the points from 3a depends on the availability of literature values available (as calculated by equation 2). Specifically, This is because the Kreiger et al data only extend to vapour pressures of the PEG series up to PEG 9.

The following has been added to the text to clarify this:

'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.'

- **Extend your experiments.** How might organic mixtures affect volatility measurements? Traditionally, pure organics are used to assess volatility, but if we use mixtures at temperatures up to 200°C, will interactions between different compounds influence volatility? Additionally, is it possible to introduce these compounds into inorganic aerosol particles to examine how inorganics impact Tmax measurement?

We agree these are very interesting questions and certainly worthy of future work, but we feel, as we have expressed in our response to a previous point, that the point of this paper is clear and the evaluation is an important first step to establish the method for single compound vapour pressure measurement before mixing of particles of different volatilities can be explored more fully in future work.

3. There is no Supporting Information for this manuscript.

We included the details of the method and the results in the main body of the paper so there is no supplementary material. None of the 3 reviewers has identified detailed additional information that should explicitly be included in supplementary material. However, two reviewers have asked for further information on repeatability and statistics of the thermograms. We will show these in the revised version of the manuscript's supplementary data. In addition, this will enable comments regarding the 'goodness of gaussian fit' of the thermograms highlighted by reviewer 3 to be addressed through the representation of repeatable results.

Minor comments:

Line 1: We can consider adding Figaero in the title. Make it more specific.

We thank the referee for the opinion on the title. The authors agree with this comment and the title has been edited to read: '*Determination of the Atmospheric Volatility of Pesticides using FIGAERO - Chemical Ionisation Mass Spectrometry'*

Line 17: I'm not sure if it's appropriate to highlight "first time" here. I wouldn't claim this is the first time particle-phase pesticides have been measured with mass spectrometry. Does the article below cover particle-phase measurements? Please verify this through a thorough literature review if you still wish to use "first time." Additionally, this phrasing may cause some confusion, as it suggests pesticides were measured in field particles, whereas the study involves measuring compounds from generated particles. In other words, as long as the vapor pressure of these compounds can be measured accurately, whether the measurements are taken online or offline is not critical to this study.

Barker, Z., Venkatchalam, V., Martin, A. N., Farquar, G. R., & Frank, M. (2010). Detecting trace pesticides in real time using single particle aerosol mass spectrometry. *Analytica chimica acta*, *661*(2), 188-194.

We would like to thank the review for the comment. The line should read Particle phase Chemical Ionisation Mass spectrometry. The authors apologise for the confusion, this has been corrected for further manuscript versions.

Line 26: A lower Tmax may be corresponded to higher measured vapor pressure?

We would like to thank the reviewer for pointing out the inconsistency. The text should read ‘*the smaller particles deposited on the FIGAERO filter compared to the aerosolised PEG calibration particles, leading to evaporation at* ***higher*** *Tmax values and a lower measured vapour pressure’* This is highlighted by equation 2 and has also been previously explained by (Bannan et al., 2019) equation 1 and the difference in particle size explored by (Ylisirniö et al., 2021), which has then been theoretically explained by (Schobesberger et al., 2018). This has been amended in future versions of the manuscript.

Line 62: Please add a citation for the sentence “In terms of current EU regulatory context, ….”

We thank the reviewer for this comment. The authors have added ‘Regulation (EC) No. 1107/2009’ as a reference. This is the legislation which details the process and requirements for a pesticide active ingredient to be allowed to be sold in the EU.

Line 78-80: We need add some citations for the sentences “there has been relatively much less attention on the fate and behaviour…”, since I believe there should be some studies in this direction.

We would like to thank the reviewer for the encouragement to delve deeper into this statement. We would like to direct the reviewer to a recent review (Brüggemann et al., 2024) which highlighted the disparity between research in the soil and water environments compared to the air. Here the limitations to understanding the atmospheric portion of pesticide transport are also explored. Further to this the review points to a few studies on the fate and behaviour of pesticide in the atmosphere (Zaller et al., 2022; Butler Ellis et al., 2021; Kruse-Plaß et al., 2021). These references begin to understand different portions and mechanisms within the environment. However, these papers additionally highlight the gaps in understanding when considering atmospheric transport of pesticide. The references mentioned here have been added to phrase mentioned in the comment above.

Line 141: Where did you find this 50%-50% definition for the C*. Please cite it. I feel this is not correct.

The following has been taken from (Donahue et al., 2006) which can be found at https://doi.org/10.1021/es052297c :

‘As an example, if C_{OA} *=1 µg* m^{-3} *and a given compound has* C_i^* *= 1 µg* $m^{-3,}$ *we would expect 50% of the mass of that compound to be found in the condensed phase and 50% in the vapor phase. In this case, any compound with (0.01≤* C_i^* *≤100) µg m-3 would have a significant mass fraction in both the vapor and condensed phases’*

The reference has been added to the definition in the updated version of the manuscript.

Line 196: A polonium source should be between CH3I flow and IMR.

We thank the reviewer for the comment, this has been corrected in future versions of the manuscript.

Here I stopped looking for more minor comments and I would like to leave future work to authors.

References

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