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Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Comparing SOA volatility distributions derived from isothermal SOA particle evaporation data and FIGAERO-CIMS measurements" *by* Olli-Pekka Tikkanen et al.

Anonymous Referee #2

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Review of acp-2019-927" Comparing SOA volatility distributions derived from isothermal SOA particle evaporation data and FIGAERO-CIMS measurements" by Olli-Pekka Tikkanen, Angela Buchholz, Arttu Ylisirniö, Siegfried Schobesberger, Annele Virtanen, and Taina Yli-Juuti

This paper describes a study that compared volatility distributions derived from direct evaporation measurements to estimates derived from measurements made using a FIGAERO-CIMS. Given the central role gas-particle partitioning plays in determining the amount of organic aerosol, this is an important topic. The FIGAERO-CIMS provides information on composition as a function of evaporation temperature but it has not been

widely evaluated in the context of figuring out volatility distribution of complex aerosols.

The paper describes a detailed analysis of previously published, relatively limited set of data – SOA formed from alpha-pinene formed in a oxidation flow reactor at two different O:C levels (low and medium). They consider low and high relative humidity and two different residence times. The very limited amount of the data is a real limitation to the paper.

Major comments/issues that broadly apply to the manuscript –

I found the paper to be a super detailed methods paper. It was not clear why it was submitted to ACP and not a journal like AMTD or AST. Based on the way the paper is written now, those journals are a better fit for the manuscript. My feeling is that while the topic of organic aerosol volatility is relevant to ACP this paper seemed is a very narrow and specialized for that journal (to me it read like a physical chemistry methods papers).

I had a hard time interpreting some the figures (e.g. Figure 2), which were often very detailed and contained many comparisons. For example, do you really need to show the three different VDevap results on Figures 2, 3 and 7 3 given they are basically the same – seems like an SI detail to help the focus the figure on what is important. This results in the paper have a bit of kitchen sink feel.

A closely related comment to the previous one, while the text described the figures and the results, I found it lacking in discussion of the results were telling us, specifically around this technique. There was too much focus on describing the data versus what the data are telling us about the technique and aerosol volatility. If it is to be accepted in ACP, I think the paper should be extensively rewritten to make it more accessible and understandable to the ACP audience. I spent a fair bit of time on the paper and got repeatedly bogged down. E.g. essentially all the tables can easily be moved to SI (maybe keep a very collapsed version of Table 1) because they are likely not of interest to a general ACP reader.

The very limited data set (a handful of conditions) seems like a pretty large limitation. Even for this limited set of data the method appears to not work so well for some conditions (e.g. low O:C in Figure 4b). There was also no discussion of experimental repeatability. There is probably enough data to justifying publication but this limitation of applying to a very narrow set of systems (and potentially overinterpreting the results) needs to be explicitly stated.

FIGAERO-CIMS – Given that it uses chemical ionization with iodide as the reagent ion as opposed to electron impact ionization, there are always concerns about mass closure. What fraction of the SOA mass is being detected by the instrument? If a large fraction of the aerosol mass that is not, then that seems like a big problem. This issue needs to be explicitly discussed, including its implications for measuring volatility. More molecular ions is a big advantage, but not measuring a large fraction of the material seems like a huge limitation as you are trying to draw inferences about the bulk aerosol based on characterizing only a limited fraction of the aerosol.

A closely related FIGAERO-CIMS concern – The FIGAERO only ramps to 200 oC (line 200). This is likely much too low to evaporate all of the SOA. Can the authors estimate what fraction of mass is evaporated? Do they account for that in any way? This issue needs to explicitly addressed in manuscript.

Uniqueness of fit – The paper takes a very empirical approach of fitting data to extract volatility distributions. That is fine and expected given the complexity of the aerosols. However, the number of data points is often quite small, comparable to the number of free parameters. For example, Figure 4 shows ~7 data points that are fit to determine VDevap. How many free parameters are in the VDevap model? Line 516 indicates that you are fitting both C* and viscosity parameters – that is a lot of free parameters given the amount of data. The fit is clearly very underconstratined. The result is that there are likely many other solutions are close to the nominally best solution. This is an optimization problem and I suspect that the optimization function looks more like a plateau then a sharp peak therefore (within experimental uncertainty) there are likely

many good solutions. While I gave one example where this occurs, this is a general issue with the paper. For example, I am concerned about the same problem for the FIGAERO PMF approach, because that also have many free parameters. Presumably all of these solutions are reasonably close across the data, but I suspect with diverge as one extrapolates away from the data. This is a major issue with these sorts of empirical approaches. The paper needs to explicitly address this issue.

Here are some specific (but not exhaustive) comments (I spent several hours on this review but was unable to sort through all the details, even though I have published a fair bit on the topic of organic aerosol partitioning).

Line 65 – The paper highlights inconsistency between growth and evaporation experiments. Ultimately C* is a thermodynamic property (certainly at the molecular level) so these inconsistencies point to changing aerosol composition or other properties. Some of this sort of framing may be useful. I.e. if the volatility distribution of the aerosol is really changing, then presumably this reflects some other changes in composition that alters the underlying C* values. Alternatively there could be issues with the kinetics of evaporation. The authors are familiar with all these issues but the introduction might be improved with this framing. To me the issue seems more fundamental then measuring a volatility distribution.

Line 327 – “matches better” Based on what quantitative metric? This is one example of a broader issue of providing quantitative metrics of goodness of fit.

Table 1 – The analysis appears to have used an accommodation coefficient of 1 to interpret the evaporation data (alpha in Table 1 versus the alpha in equation (3)). This was not discussed or justified (none of the values were in Table 1 were justified). There are papers that report smaller values for this system (e.g. Saleh et al. Env. Sci. Tech. 2013). How would reducing this value alter the results from the analysis? This should be discussed in the paper.

Figure 2 indicates little agreement in the “raw” volatility distributions between the PMF and evaporation approach. This is mentioned but not discussed in the text. The figure is also very confusing since there are overlaps in the volatility of the different PMF factors (i.e. one you don't show a volatility distribution of the PMF factors). I think it would be much clear if you lumped the factors together into a volatility distribution, using the colors to indicate the contribution of each factor to each bin (i.e. the volatility distribution would have stacked colored bars).

Compared to Figure 2, there is better agreement in Figure 3 when the offers have lumped in the material into larger bins wider than one order of magnitude. That seems encouraging, but this lumping process and its justification was not \discussed in the text. How different are the evapograms (Figure 4) when you use these different representations? A key issue is what level of information is there in the data. As I have discussed in earlier comment this problem seems very under constrained given the amount of data they have collected.

Line 109 – What compounds were used to calibrate Tmax? The paper should provide a calibration curve showing these results.

Figure 4 – It is interesting that the PMF approach performs better for the medium O:C aerosol compared to the low O:C aerosol. The PMF approach overestimates the evaporation of the This is mentioned on line 327, but only briefly discussed (~ line 500). The authors speculate it may be due to viscosity or particle phase chemistry. It would be good to think about whether this indicates a shortcoming of the approach. For example, could this be due to the CIMS not detected a larger fraction of the less oxygenated aerosol? (This is related to some earlier comments).

Figure 8. Optimized results (around line 440). The agreement seems impressive, but I suspect this is a just the result of fitting a model with lots of free parameters to a small set of data. Therefore, I am not surprised that the fit is great. If the fit is under constrained is this telling us anything about the technique? It was not clear if the authors had tested the applicability of the extracted values from this optimization

against data the model had not been fit to? If this optimization is to be presented these issues must be discussed and some sort of cross-validation presented.

Figure 8 –I interpret the dashed lines as the range of predications for the FIGAERO based approach (i.e. using the "theory" to predict viscosity). Is that correct? It is hard to tell what comparisons are based on truly independent comparison just using the FIGAERO versus fits of the data.

Figure 8. Can't differentiate between grey and black dashed lines.

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