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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Optimization of process models for determining volatility distribution and viscosity of organic aerosols from isothermal particle evaporation data" *by* Olli-Pekka Tikkanen et al.

Anonymous Referee #2

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In the study at hand, Tikkanen *et al.* give a very detailed description of their process to extract important physical properties of organic aerosol particles, namely volatility and viscosity, from laboratory data. This is achieved by inverse fitting of a process model that describes all relevant physical processes in a typical laboratory system. In the first part of the manuscript, the authors compare two algorithms for optimization of process model input parameters in their performance in obtaining parameters they had earlier used to generate artificial data. The two algorithms are (i) a modified/improved implementation of a method that has been previously established in their field (MCGA

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Discussion paper

algorithm) and (ii) the canonical method of Bayesian inference. In the second part of the manuscript, the MCGA algorithm is evaluated in more detail by applying it to scenarios that would typically occur in laboratory experiments designed to determine the volatility and viscosity of mixtures of more or less known composition. In their meticulous study, the author's outline several pitfalls in this process, which is of great value for future investigations. This fundamental work is of high importance for the Atmospheric Chemistry and Physics community and hence fits well within the scope of ACP. The manuscript is well written and I will have no concerns about publication of this paper after the following general and specific comments are addressed.

General Comments

1. It is noteworthy that the authors do not use numerical values of their measure of model result-data correlation (*fitness*) for their argumentation. The performance of an optimization algorithm should also be evaluated in terms of how quickly (or how reliably) it reaches a certain threshold of model result-data correlation that justifies consideration of the optimized parameter set (e.g. model result-data residue is comparable to the noise in the experimental data). The authors denote the spread in fitted parameters, but it would also be interesting to see spreads in their measure for correlation, especially in section 3 where two methods are compared.

2. What is the reason to choose MCGA over Bayesian inference for further analysis in this manuscript? Did one method outperform the other in any regard or was it just easier to operate?

3. I wonder how big the error is that is introduced by combination of the topmost bulk layers in the KM-GAP model during evaporation. This practice in conjunction with discrete layers can introduce step-profiles in evaporation, where evaporation slows down as volatile constituents are depleted from the topmost bulk layer and

picks up pace again as soon as layers are merged (and hence volatile component is mixed into the topmost bulk layer). Kinetic models operating with fixed layer sizes and merging schemes have to have mechanisms in place that prevent these artifacts from happening, especially when input parameter optimization is automatized and hence numerical convergence not always manually checked for each combination of input parameters. Which mechanisms are in place in this study to prevent this?

4. A stylistic suggestion: A concept that is usually used when talking about model parameter optimization is that of a parameter's (local) sensitivity. Talking about conditions under which model output is sensitive to the numerical value of an input parameter could simplify the (sometimes a little slow-moving) discussion in this manuscript considerably. However, usage of this concept is left to judgment of the authors.

Specific Comments

1. Sect. 1, l. 45 – What do you mean by "increasing attention has also been given to modeling the particle dynamics to better understand the measurements"? Particle dynamics could refer to processes like deposition and coagulation, but probably means evaporation dynamics here, please clarify.

2. Sect. 1, l. 50 – The literature review on kinetic parameter determination through inverse modelling seems a little sparse here. Even in aerosol research, there have been more studies detailing such procedures. Examples include Berkemeier *et al.* (2016), who determined both diffusion coefficients and reaction rates by inverse modelling or Lowe *et al.* (2016), who used a Monte Carlo Markov Chain (MCMC) algorithm on artificial data as a tool for sensitivity analysis.

3. Sect. 2.2, l. 132 – It is counterintuitive to talk about a good candidate having

low fitness here since in the biological sense a high fitness would be considered better. “Fitness” is thus usually defined as the inverse of least-squares deviation.

4. Sect. 2.2, l. 153 – Can you expand on why the Metropolis criterion ensures variability in the population? While this might be intuitive for experts, it might not be for clear to the general reader of ACP. A couple of follow-up questions on the Metropolis algorithm: Did the MCGA algorithm perform significantly better with this criterion? Do you make sure that a newly created parameter set with improved fitness over all previous ones is not discarded?

5. Sect. 2.3.1, l. 201 – The comment on subconscious bias made me wonder what choices the person performing the optimization has. In my understanding, there should be none in a fully automated optimization.

6. Sect. 4, l. 294 – Please define the term “optimization rounds”. From context, it seems to be completed MCGA runs. In contrast, how many process model evaluations were performed in each MCGA run? How has this number been chosen?

7. Sect. 5.3 – You give two potential reasons for the process model failing at describing the experimental data using only literature values for viscosity and volatility. Can you add a brief discussion on what you think contributes more to the observed discrepancy, the depressed viscosity or hindered evaporation due to Raoult’s law?

8. Sect. 6, l. 600 – “(. . .) the few shortcomings of the method could be largely attributed to the fact that the method can only characterize properties that influence the quantity that is measured”. As stated, this is too trivial, please rephrase. You may want to refer to it as “model parameters that have sufficient sensitivity in the probed time and concentration range”. For reference, some general concepts of model parameter optimization (at least for application in aerosol research) have

been discussed in section 3 in Berkemeier *et al*. (2017) or can be found in the discussion of sensitivity analysis and kinetic regimes in Berkemeier *et al*. (2013), section 6.

9. Fig. S9 – Please add literature values from Table 5 into the plot since you are referring to this comparison in Sect. 5.3.

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