

Interactive comment on “Estimation of the volatility distribution of organic aerosol combining thermodenuder and isothermal dilution measurements” by Evangelos E. Louvaris et al.

Anonymous Referee #1

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The authors report on two experiments from a “new experimental method” that is really a combination of two existing methods: a thermodenuder and a dilution chamber. They use the model of Karnezi et al. (2014) to analyze the observations and extract volatility distributions for organic aerosol generated from meat charbroiling. The current study adds an explicit experimental element that was absent from the theoretical Karnezi et al. study. Given that the primary difference between this study and the Karnezi et al. study is the experimental measurement, I think that the manuscript requires much more detail regarding the experimental setup and what makes this new. Also, I think that the authors need to do a more complete job with data quality assurance, or at least need to convince me that their dilution measurements are correct. Finally, I think that

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the authors need to give more appropriate credit to work that has come before this. With substantial revision, I think that this paper could be acceptable for publication.

Specific comments follow below.

In their introduction, Louvaris et al. completely downplay the similarity of their work to the previous work of Grieshop et al. (2009, ES&T). The title of the Grieshop paper is “Constraining the Volatility Distribution and Gas-Particle Partitioning of Combustion Aerosols Using Isothermal Dilution and Thermodenuder Measurements.” This is extremely similar to the title of the current paper: “Estimation of the volatility distribution of organic aerosol combining thermodenuder and isothermal dilution measurements.” In the introduction, the authors mention that “Volatility measurements [by Grieshop] based on longer equilibration timescales were performed for POA from a diesel engine and wood combustion using isothermal dilution.” But, they do not even mention that Grieshop also performed thermodenuder measurements. This seems to me like intentional obfuscation, especially since the authors also note that “Karnezi et al. (2014) proposed that volatility distribution of complex OA can be better constrained combining TD and isothermal dilution measurements,” and later “we develop a new experimental technique to constrain the volatility distribution of organic aerosol using TD combined with isothermal dilution measurements following the suggestions of Karnezi et al. (2014).” Why mention Karnezi but not Grieshop in this context? Simply because one of the authors here is a co-author on the Karnezi paper but not the (earlier) Grieshop paper? I am concerned about this clear, seemingly intentional downplaying of previous measurements and methods.

The dilution experiments are insufficiently described. Was aerosol transferred once to the dilution chamber and then air sampled from it while the bag was allowed to collapse? Or was make up air continuously added? What was the flow rate through/out of the bag?

Comparison of Fig. S3 and S4 indicates that for Experiment 2 the “corrected” number

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loss is ~10-15% and, importantly, is very similar to the “corrected” mass loss. In other words, comparison between these figures suggests, at least to me, that the mass loss is entirely driven by number loss for this experiment. I have similar concerns regarding the dilution data for experiment 1, from comparison between Fig. S2 and Fig. S6. Put another way, it seems that the number-normalized mass loss for the dilution experiments is close to zero (MFR close to 1). To be convincing that the mass loss is real, I think that the authors need to consider the extent to which the particle size distribution shifted. Was shrinkage observed to an extent that is consistent with 10-15% mass loss? Currently, I do not find the “corrected” mass loss experimental observations convincing. Consequently, I have concerns over the resulting model interpretation of the observations and the entire paper.

L109: Since the authors are looking at “fresh” OA, it is unclear why OH radical concentrations are mentioned. D9 butanol is simply used as a dilution tracer.

L206 and Fig. 5: The experiments took nearly 8 h (30 mins at each of 15 temperatures). I think that the authors need to provide more information regarding exactly when the various spectra were measured. Is the “ambient” spectrum an average over those ~8 h? Is it the average of the two measurements that came before/after the 200 C measurement? How similar in time was the ambient spectrum to the 200 C spectrum? Related, how similar were the ambient spectra measured at the beginning of the measurement versus 8 h later at the end of the measurement? Have things evolved over time due to the particles being suspended in the chamber? Granted, the spectra are quite similar, as the authors note, but more detail is required. Further, the authors simply note that the spectra are similar. But, their calculations suggest that, perhaps, they should be different because the particle composition at ambient vs. 200 C is different. This should be discussed.

L217: The authors note that there are “small” differences between the two experiments. But I would argue that the differences, especially in the TD experiments, are actually quite large. I have included the figures from the paper below so that they can be

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directly compared. It is clear that the behavior at lower temperatures is dramatically different. One experiment indicates almost no evaporation until $T > 80$ C while the other indicates substantial (20% loss) evaporation at temperatures just over ambient. Further discussion is required.

L307 and elsewhere: The authors report the “average” volatility in a number of locations. First, it is not clear how this is calculated. Is it a linear average? A logarithmic average? Second, in reporting this number the authors seem to be making an a priori assumption that this is a meaningful number. This is not a value that is commonly reported. What is this mean meant to represent and how is it useful? I could have two very different distributions, for example one bimodal and one monomodal, that have the same average. These would exhibit very different behavior though.

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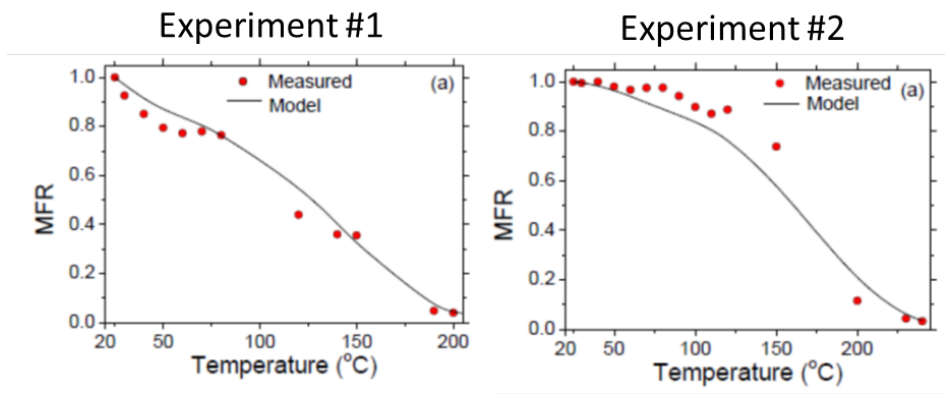


Fig. 1.