

Interactive comment on “Measuring the atmospheric organic aerosol volatility distribution: a theoretical analysis” by E. Karnezi et al.

E. Karnezi et al.

spyros@chemeng.upatras.gr

Received and published: 31 May 2014

Comment: *This paper presents work in an important area of considerable current interest. The retrieval of volatility distributions from thermodenuder measurements is reliant on a number of assumptions and is subject to uncertainties in a range of parameters. The manuscript attempts to investigate a number of these uncertainties using a reasonably appropriate combination of modelling approaches with error propagation to conclude that the particle volatility distribution is underconstrained. The authors then propose a combination of dilution and heating as an improvement to using a thermodenuder alone, as previously suggested and demonstrated by Grieshop et al., 2009. The work is largely well-conceived and the problem appropriately framed in terms of the*

C1137

literature up until early 2011. Thereafter, much literature directly of relevance to the current work has been ignored (e.g. Cappa Wilson, 2011; Fuentes McFiggans, 2012; Saleh et al., 2011; 2012 and later citing references, amongst others). The area has developed considerably since the most recent literature on thermodenuders cited in the current work. It is a little unfortunate that the authors are apparently unaware of these studies which previously investigated many of the questions in the current manuscript (in some cases in greater depth and quite robustly). This is particularly surprising, since one of the authors also co-authored a recent paper that cited the first three papers listed above (Hakkinen et al., ACP, doi: 10.5194/acp-12-10771-2012, 2012). The lack of recognition of literature is quite troubling throughout: the suggested combination of dilution and heating as constraint on a volatility distribution is not novel, but the Grieshop et al. (2009) paper where it has been demonstrated was again uncited. I understand that this is a theoretical analysis, but there is no reason not to recognise where the technique has been applied experimentally. Whilst the application and some of the conclusions of the current work have some novelty, I feel that it would be in the authors and the broader community's interests for the manuscript to be framed in terms of the recent directly relevant literature. The authors should especially identify the particular areas of novelty of their work in the context of this literature and where their approach confers new insight or advantage over previous work. I am not saying that the current work has no value, just that it is hard to take it seriously when conducted in an apparent vacuum. I was close to recommending outright rejection, but there is valuable work included in the manuscript. I would be happy to re-review a resubmitted paper in which the novelty were more easily identified and contextualised.

Cappa, C. D. Wilson, K. R., Evolution of organic aerosol mass spectra upon heating: implications for OA phase and partitioning behavior, Atmos. Chem. Phys., 11, 1895–1911, doi:10.5194/acp- 11-1895-2011, 2011.

Fuentes, E. McFiggans, G., A modeling approach to evaluate the uncertainty in estimating the evaporation behaviour and volatility of organic aerosols, Atmos. Meas.

C1138

Tech., 5, 735–757, doi:10.5194/amt-5-735-2012, 2012.

Grieshop, A. P. et al., *Constraining the Volatility Distribution and Gas-Particle Partitioning of Combustion Aerosols Using Isothermal Dilution and Thermodenuder Measurements*, *Environ. Sci. Technol.*, 43 (13), 4750–4756, doi: 10.1021/es8032378, 2009.

Saleh, R., Shihadeh, A., Khlystov, A., *On transport phenomena and equilibration time scales in thermodenuders*, *Atmos. Meas. Tech.*, 4, 571–581, doi:10.5194/amt-4-571-2011, 2011.

Saleh, R., Khlystov, A., Shihadeh, A., *Determination of evaporation coefficients of ambient and laboratory-generated semivolatile organic aerosols from phase equilibration kinetics in a thermodenuder*, *Aerosol Sci. Technol.*, 46, 22–30, 2012.

Response: There is clearly a rich literature on thermodenuders. There have been more than 100 papers published during the last 5 years with some form of analysis of thermodenuder data. We did our best to cite what we considered the most relevant pieces of work. We could have obviously cited more. This applies to almost every paper published these days given the explosion of the publication activity in the atmospheric aerosol field. More specifically for the papers mentioned by the reviewer:

(a) The paper by Grieshop et al. (EST, 2009) was actually cited and discussed in pages 863–864 and 875. This is clearly the basis for part of the current work, because it was the first to suggest the combination of thermodenuder measurements and isothermal dilution. The misunderstanding by the reviewer was probably caused by the fact that there were two Grieshop et al. (2009) papers and while both of them are discussed in the paper only one of them (the ACP paper) was in the reference list. We have added the missing reference to the list. The current work goes far beyond the Grieshop et al. (ACP, 2009) paper because it quantifies the benefit of the combination of the isothermal dilution and thermodenuder measurement for the accuracy of the estimated volatility distributions and the other parameters.

C1139

(b) We had cited in the original paper the Cappa (2010) and Cappa and Jimenez (2010) publications presenting the efforts of these authors to model the evaporation kinetics of organic aerosol in a thermodenuder and to retrieve the organic aerosol volatilities from these measurements. The Cappa and Wilson (2010) paper mentioned by the reviewer focused on the evolution of organic aerosol mass spectra from lubricating oil and SOA from α -pinene ozonolysis upon heating. One of their major conclusions was that they observed significant mass transfer delays during the evaporation of the α -pinene SOA. We have added this reference to the revised paper.

(c) References to the Saleh et al. (2011; 2012) papers have also been added. Saleh et al. (2011) developed a thermodenuder model and used it to estimate the corresponding equilibration time scales. Saleh et al. (2012) developed a method combining a particle concentrator and a thermodenuder to measure the effective evaporation coefficient of ambient aerosol. Their measurements suggested only small mass transfer delays (coefficients of around 0.3) for the ambient aerosol that they examined.

(d) The Fuentes and McFiggans (2012) paper is quite complimentary to the current work and should have been referenced in the original paper. This omission has been corrected in the revised paper. The authors address a number of topics in their analysis including the need to simulate the dynamics of the thermodenuder system and not to assume equilibrium, the potential problems that can be caused by recondensation in the cooling section of a thermodenuder, the experimental challenges in dilution chambers due to wall effects, and the mass transfer delays in the evaporation of α -pinene SOA.

The addition of the above references and the corresponding discussion does not change the framing of our work in the context of the rest of the literature. This is the first effort to systematically quantify the error and uncertainty of the retrieved parameters (volatility distributions, enthalpy of evaporation, mass accommodation coefficient) from thermodenuder measurements of ambient aerosol. We show that these values are quite uncertain (more than we at least expected) and that often the best fit does not

C1140

correspond to the most accurate estimate. We propose a new method to estimate an ensemble of solutions and use them to derive a best guess and more importantly an uncertainty range. Given that the corresponding uncertainties are quite high, it is clear that additional measurements are needed. We tried a number of potential solutions and recommend the combination of isothermal dilution and thermodynamic measurements. Our approach for the estimation of the parameters and the corresponding uncertainties is applicable to this combination of measurements too. We stress the above points in the revised conclusions sections, to make sure that they are appreciated by the readers.

Interactive comment on Atmos. Meas. Tech. Discuss., 7, 859, 2014.

C1141