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Atmospheric Measurement Techniques Discussions

Interactive comment on "A modeling approach to evaluate the uncertainty in estimating the evaporation behaviour and volatility of organic aerosols" *by* E. Fuentes and G. McFiggans

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The manuscript describes modeling of processes occurring in a thermodenuder (TD). Unfortunately, the authors make a major mistake by using an erroneous wall boundary condition in the cooling section of TD, which necessitates revising all of the calculations and conclusions presented in the manuscript. Further, the manuscript ignores the analysis presented in our recent paper (Saleh et al. 2011. On transport phenomenon and equilibration time scales in thermodenuders," AMT, 4, 571-581, http://www.atmos-meas-tech.net/4/571/2011/amt-4-571-2011.pdf). Our paper resolves in a more definitive manner many of the questions explored by the authors of the current paper, provides the key dimensionless parameters that connect the myriad variables that concern the authors, and debunks using theoretical, modeling, and experimental evidence many of the conventions used in this manuscript. For example, we showed that use of the "mass fraction remaining" (MFR) is problematic for characterizing aerosol volatility because any MFR can be obtained for a given aerosol by simply varying the initial mass loading. The correct measure that is uniquely related to volatility is the change in mass concentration across the thermodenuder. Similarly, we showed that equilibration time is not a function of aerosol mass loading but rather aerosol length. While the authors of the current manuscript cite our recent paper, they provide no arguments as to why they ignore these findings and continue to employ problematic constructs. Our paper is the only one published on the subject that combines all three aspects of the analysis. The theory and the model presented in our paper agrees exceptionally well with the observations. We provide a comprehensive dimensionless theoretical analysis which covers the topics presented in the current manuscript, including equilibration time scales, re-condensation in the cooling section and the role of activated carbon in the cooling section. The dimensionless analysis allows us to draw general conclusions, which are valid for any denuder design, any aerosol loading, size distribution and accommodation coefficient. In contrast, the current manuscript is limited to a single denuder design and only a few aerosol parameters. Yet, the authors claim generality based on a very limited number of simulations. The authors need to correct the wall boundary conditions, re-do the calculations and re-evaluate all of their conclusions. If the conclusions are different from those in Saleh et al. (2011), the authors will need to explain why their model results contradict what follows from the theory on which their model is based.

Specific comments:

6726/2: In Saleh et al. (2008), equilibrium is not "assumed", it is experimentally verified.

6726/6-9: Please note that Riipinen et al. (2010) does not contain any theoretical analysis, as can be verified by reading that paper. A rigorous theoretical analysis of the processes can be found in Saleh et al. (2011).

6726/8: It is true that Riipinen et al. (2010) came to a conclusion that compound volatility influences equilibration time. This is, however, an erroneous conclusion based on incorrect criteria for the model to declare the system to be in equilibrium. See Saleh et al. (2011) for explanation of this error and theoretical, modeling and experimental evidence that the equilibration time does not depend on aerosol volatility.

6727/5 and 7: a better reference would be: Saleh R., Khlystov A., Shihadeh A. (2012) Determination of evaporation coefficients of ambient and laboratory-generated semi-volatile organic aerosols from phase equilibration kinetics in a thermodenuder. Aerosol Sci. Technol., 46, 22-30.

6728/5-11: Saleh et al. (2011) presented not only measurements, but also detailed theoretical and modeling evidence which was in a very good agreement with experiments. It should be also noted that the model used in Saleh et al. (2011) treats heat and mass transfer, is size resolved and uses size distribution measurements as its input. The model has been verified against a size-resolved model, which solves explicitly a set of coupled PDEs for heat and mass transfer under laminar flow profile using the MATLAB PDE solver (Khlystov et al. 2009). In contrast, model by Cappa (2010) uses one particle size and does not solve for heat transfer, using instead a predefined temperature profile without radial temperature gradient. This approach is especially problematic in the cooling section, where the vapor removal scales with the cooling rate. In any case, the more detailed model by Saleh et al. (2011) and its results need to be presented as a counterpoint to Cappa (2010).

6731/Eq.4 and the following text: This is a wrong boundary condition for the cooling section. The authors use a boundary condition dCi(x,R)/dr = 0, i.e. no material flux to the walls (Eq.4 and page 6731, lines 14-16). This boundary condition is correct for the heated section after the walls have been equilibrated with the gas stream. However, it

is clearly wrong for the cooling section, which can be easily verified by commonplace observations of water vapor condensing on cold surfaces. The same phenomenon happens in the cooling section of a thermodenuder: hot saturated species condense on the colder walls of the cooling section. This has been experimentally observed in TD measurements too (Saleh et al., 2011). The correct boundary condition at the walls of the cooling section is C(x,R) = Csat(Twall), i.e. the species concentration at the wall boundary should be equal to its saturation concentration at the temperature of the wall or the equilibrium partial vapor pressure at that temperature if one works with mixtures.

In the cooling sections the gas stream cools and becomes supersaturated. Due to the wrong boundary condition in presented model, however, it has no other place to go but condense onto the particles. It is not surprising then that the authors obtain strongly exaggerated re-condensation fractions. In real life, however, walls present a very strong and mostly dominant competition to gas condensation, even at high aerosol loadings, allowing only modest re-condensation fractions (Saleh et al., 2011).

Also, the denominator in Eq.4 should be dr, not dx.

6732/Eq.10 and lines 22-23: I do not understand this equation and how there could be “no heat losses in the system”. If there are no heat losses, there should be no cooling and thus no condensation to particles or the walls.

6733: I do not agree that a plug flow profile is a better approximation than the parabolic profile. The fraction of the flow that is near the wall is negligibly small and should not affect the vapor gradient if the mass balance is preserved. Furthermore there appears to be a contradiction in utilizing a plug flow velocity profile while at the same time allowing for radial gradients in temperature and vapor concentration.

6735/13-17: RF used in this study is defined in a different fashion than in Saleh et al., 2011. In Saleh et al. (2011) RF is the maximum amount of vapor that can re-condense in the cooling section (i.e. IF the aerosol reaches equilibrium in the cooling section) divided by the amount of vapor that has evaporated from the particles in the heating section.

Section 4 and further: All calculations need to be redone with the correct boundary conditions and conclusions reevaluated.

6738/1-19: Please note that Saleh et al. (2011) provides the equilibration parameter, which combines the effect of particle size, number concentration and accommodation coefficient to estimate the equilibration time.

6739/9-16: Please note that the accommodation coefficient of succinic acid derived by Riipinen et al. (2006) is for an aqueous solution, while that for adipic acid derived by Saleh et al. (2011) is for solid particles. Accommodation processes of molecules to solid and liquid particles are fundamentally different and cannot be compared as the authors do. It should be also noted that the value for adipic acid has been confirmed by a different method that uses a combination of equilibrium and TDMA measurements (Saleh et al., 2009). Also, what value for Csat do the authors use in their simulations? If one uses a Csat value obtained from a study which assumed accommodation coefficient of 1 (e.g. TDMA, TPD, EDB, etc.), then it is no surprise that their model predicts an accommodation coefficient of 1.

6740/1-17: Saleh et al. (2011) provides a fairly simple dimensionless parameter to estimate the re-condensation fraction, which is a function of not just the residence time, but also of the diameter of the cooling section. One cannot separate the effect of these two parameters on the re-condensation fraction. Thus, all the discussion in this paragraph, which revolves around residence time in the cooling section, is meaningless. Further, the dimensionless parameter given in Saleh et al. (2011) is applicable to ANY thermodenuder design. Thus, the claim that findings of Saleh et al. (2011) cannot be extrapolated to other studies is simply wrong. In fact, the claims made by the authors are only applicable to the TD design that they model and thus cannot be extrapolated to studies using other TD designs. For example, Huffman et al. (2008) use a 1.9 cm ID cooling section, while the authors use 2.2 cm in their model (Fig.1). Ann et al. (2007) use 3.5 cm ID cooling section. All of these will give different results due to the different ratios of residence time to the wall area. As is shown in Saleh et al. (2011) activated carbon denuder does not necessarily prevent re-condensation in the cooling section. In fact, initially, the re-condensation fraction is identical to that without activated carbon (see Fig.8 in our paper). This proceeds until most of the excess (relatively to equilibrium with the walls) vapor is stripped by the walls, after which point the denuder starts distilling the material from the particles, eventually leading to negative re-condensation fractions with all the negative consequences for deriving volatility distributions from the measured data.

6743 and the following pages: It should be noted that equilibrium is impossible in an enclosed system if the Kelvin effect is taken into account: the vapor pressure over particle surface will be always higher than that over material-coated walls of TD. However, under the usual residence times in TD, the effect of curvature on deviation from equilibrium is relatively small for most aerosol systems. For this reason the Kelvin terms should be dropped from the analysis. If Kelvin effect is substantial, the equilibrium assumption, which is implicitly used in the analysis, fails invalidating the formulas derived by the authors.

6744/10 and the following: Please check equation numbering

6744/Eq.12: Delta Cp,i should be negative in this equation.

6747/16 and further: “functional groups” should be “homologous groups”.

6748/5-10: the expression derived in the current manuscript for pure components could be more accurate than that in Foulhaber et al. (2009). However, a simpler formula provided by Saleh et al. (2008) would be preferable, because it does not require one to use high temperatures necessary to achieve T50 at high aerosol loadings, which are necessary for aerosol equilibration.

6748/11: Saleh et al. (2011) also shows that it is impossible to equilibrate aerosol in

TD at ambient concentrations.

6749/10-12: This is true only if the same thermodenuders are used, not “different” ones. It is obvious that different residence times in the heated section and different diameter/lengths of the cooling section can potentially produce different results even for a single component aerosol. Regarding the surrounding discussion, it should be also noted that Eq.25 is useful only when the initial aerosol composition is known, i.e. Xi,0 are known. Unfortunately, the main purpose of thermodenuders is to elucidate the unknown volatility distribution of the test aerosol. For an unknown aerosol, Eq.25 is of little use, because there is an infinite set of combinations of Xi,0 that provide the same MFR in the same denuder and at the same initial mass loadings. If one includes variations in denuder design and the variation of initial mass concentration of ambient aerosol, the picture becomes completely indecipherable. MFR is a very poor way of expressing aerosol volatility.

6749/18: I do not understand how these formulas, which were derived with MFR explicitly included, could be of any use for any process in which initial concentration is not preserved. As Saleh et al. (2011) show, and what is also obvious from the formulas in this manuscript, MFR is meaningless for comparisons of observations made at different aerosol loadings. Convective lifting involves expansion, which necessarily leads to a change in the initial mass concentration as expressed in the MFR, invalidating all these formulas.

6750/3 and further: I do not understand how formulas that were derived using equilibrium Clausius-Clapeyron equation could be used for non-equilibrium conditions.

Section 7.2: As the authors rightly point out, kinetic processes are all strongly size-dependent. It is a well-known fact that ambient aerosol is polydisperse. Could the authors comment on how adequately a single size kinetic model, as the one used in the manuscript, represents such a system?

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