Response to Dr. Khlystov's Comments on manuscript "A modeling approach to evaluate the uncertainty in estimating the evaporation behaviour and volatility of organic aerosols "
by E. Fuentes and G. McFiggans.

Summary. We thank Dr. Khlystov for his interest in our manuscript and his unsolicited helpful comments and suggestions. Comments by Dr. Khlystov mainly focus on the particular area of the manuscript based on the study on re-condensation and on discrepancies with respect to results in Saleh et al. (2011). His main criticism is that we have not considered a boundary condition for wall equilibrium condensation in the cooling section. This, in his opinion, should lead to an excessive particle growth in the cooling section and overestimation of re-condensation in our model. Our previous calculations using a boundary condition of no mass transfer to the walls provide an upper estimate for the potential re-condensation in the cooling section. We agree that an equilibrium wall condensation boundary condition, which represents a lower estimate for re-condensation, should also be considered, as the condition of no mass transfer to the walls may not always be realistic. Our recalculations using this boundary condition show that although the degree of re-condensation is somewhat lower than previously estimated, re-condensation is still significant at high aerosol loadings (Figures **R1** and **R2** in this response). Hence, our previous conclusion that re-condensation may significantly affect thermograms holds even for the lower estimate implied by the assumption of equilibrium wall condensation. We should note that a discussion on the influence of wall local conditions on re-condensation has already been addressed in the open discussion of Cappa (2010) (http://www.atmos-meas-tech-discuss.net/2/C1209/2010/amtd-2-C1209-2010.pdf). Regarding this issue, we consider, as Dr. Cappa, that a condition of equilibrium at the wall is an assumption that will not necessarily be attained, and that both lower and upper estimates should be considered to derive the potential for re-condensation. It should however be noted that because we aim to quantify the maximum deviation induced by re-condensation, it is the upper estimate that we previously presented that is important for our study of uncertainty. In the revised paper we will include the results for lower and upper estimates for re-condensation under the limiting conditions of no mass transfer to the walls and equilibrium wall condensation. We will include a new Figure in the supplementary material showing lower estimates for re-condensation at different aerosol mass loadings (Figure R1, bottom) and will also add curves for lower estimates of re-condensation in the parametric analysis of the revised manuscript and the final plots showing volatility distributions. Because some figures already include a large number of curves, we will not add extra data on lower estimates to all graphs (eg. Fig. 8 and 9); however, we will revise the text where the lower estimate may affect our interpretation of thermograms. In those cases in which only the upper estimate is presented, this will be clearly stated in text and figures.

The significant re-condensation degree that we have obtained for the lower estimate of re-condensation is a result of the geometry and experimental conditions of the thermodenuder (TD) designs simulated in our study. The dimensionless number Cn in our parametric simulations ranged from 2.7-10, which is well above the maximum value of Cn=0.7 established by Saleh et al. (2011) for negligible re-condensation. Hence, there is no disagreement between our results and those in Saleh et al. (2011). In our study we have worked with geometries and conditions representative of some currently used TD designs, such as Huffman et al. (2009), which presents Cn values much higher than 0.7 at high aerosol loadings (eg. Cn=2-7.4 for 100 nm particles at 400 μg/m3 and C*=0.01 μg/m3). Although we acknowledge that TD geometries could potentially be modified to reduce the effect of re-condensation, the aim of our study is to analyse the problems derived when using existing TD systems, even if their geometries are not optimum to minimise re-condensation issues. We will make this clear in our revised version of the paper. Finally, Dr. Khlystov's is concerned about our use of "problematic constructs", i.e. thermograms, for deriving volatility information. It is true that volatility information cannot be inferred from the simple comparison of MFR (mass fraction remaining) values because of their dependence on the initial aerosol loading; however, as shown in our work and elsewhere, thermograms can be used to infer volatility information with the aid of methods accounting for the influence of the initial aerosol mass loading. The validity of our approach is supported by previous literature making use of these methods (eg. Faulhaber et al. (2009), Cappa and Jimenez (2010)) and comparison with volatility information from other studies (eg. Figures 14-16 in our manuscript). We should also point out that, in our support, reviewer #1 does not agree with this argument by Dr. Khlystov (please, see comment 29 by reviewer #1).

Below we include detailed responses to all comments (*Dr. Khlystov's comment (blue and italic),* authors' response (black))

1) *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.*

In this comment, Dr. Khlystov points out that we have neglected a boundary condition accounting for the condensation on the walls of the cooling section and that this may have a significant effect on the results and conclusions of our study. Our previous calculations using a boundary condition of no mass transfer to the walls provide an upper estimate for the potential re-condensation in the cooling section. We agree that an equilibrium wall condensation boundary condition, which represents a lower estimate for re-condensation, should also be considered, as the condition of no mass transfer to the walls may not always be realistic. As suggested, we have made new calculations including this condition with Cg,i(wall)=x,i Csat,i(Twall))). In Figure **R1** we present our previous results for upper estimate and new results for lower estimate of re-condensation. Our new calculations show that although the particle growth is lessened as a result of gas condensation on the walls of the cooling section, there is still significant re-condensation occurring at high mass aerosol loadings, with respect to the exit of the heating section. This affects our definition of the minimum aerosol mass loading for which re-condensation may be significant (i.e. RF>20%), with a new value of 50 μg/m3 versus our previous value of 30 μg/m3; however, this does not change our conclusion that re-condensation is substantial at high aerosol loadings for the TD design under study, even for the lower estimate implied by the assumption of wall condensation equilibrium conditions.

The inclusion of the wall condensation boundary condition also affects our results on the performance of the charcoal denuder. Figure **R1** in this response shows that, under the assumption of equilibrium wall condensation, a charcoal denuder is of no use in reducing re-condensation for compounds of low volatility. As in Saleh et al. (2011), this is due to the gas concentration Cg being much higher than Csat(Twall), thus leading to similar gradients between the gas phase and the walls in the cooling and denuder sections (i.e. Cg-Csat(Twall)~Cg-0). We have found that using a charcoal denuder is of no benefit for volatilities up to 1 μg/m3. For volatilities above this value (Figure **R2**), the charcoal denuder becomes slightly more efficient to avoid re-condensation, however it induces particle evaporation below 45°C. As mentioned above, these results represent a lower limit for re-condensation, as the equilibrium conditions at the walls may not be achieved in all cases; thus, the charcoal denuder may still be useful at conditions where equilibrium on the walls is not attained.

The assumption of wall condensation also lessens the significance of re-condensation in affecting the volatility distributions derived from thermograms for a-pinene SOA in section 7. We have redone cooling section calculations including this boundary condition in sections 4 and 5 of our study and reanalysed the volatility distributions which were affected by re-condensation in section 7. Because a condition of equilibrium at the wall is an assumption that will not necessarily be attained, we believe that both lower and upper estimates should be considered to derive the potential for re-condensation. We will present the results for upper estimate (no absorption to the walls) and lower estimate (wall condensation equilibrium) of re-condensation in the revised version of the manuscript.

2) *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.atmosmeas-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.*

We disagree that our present manuscript ignores the analysis presented in Saleh et al. (2011). The only particular area in common between our study and Saleh et al. (2011) is the analysis on the re-condensation issue, presented in sections 4 and 5 of our manuscript. While Saleh et al. (2011) summarise their calculations on a single representation, showing re-condensation fractions (RF) as a function of a dimensionless number comprising the parameters affecting re-condensation, we developed a parametric analysis to evaluate and illustrate the effect of each of these parameters on re-condensation. Saleh et al. (2011) claimed that negligible re-condensation is expected for the "vast majority" of thermodenuder geometries, at both ambient and laboratory measurement conditions and that charcoal denuders are of no significance in reducing re-condensation. In our study we have tested whether these claims apply to a number of typical thermodenuder geometries currently in use (eg. Huffman et al. (2008), Grieshop et al. (2009)) and have found that re-condensation can still be important for these common designs. Also, while Cappa (2010) shows that the potential for re-condensation will depend on the particular local conditions at the walls, Saleh et al. (2011) generally claim that re-condensation is negligible for most TD designs and experiments; thus, further study on this area is justified. On the other hand, experiments in Saleh et al. (2011) showing negligible re-condensation cannot be extrapolated to other conditions, due to their short residence time (1.87–3.74 s.) compared with residence times in commonly used systems (eg. 15.5 s. in Huffman et al. (2009)), and also, because these measurements were conducted with aerosol samples presenting low accommodation coefficients (<=0.1), conditions which would lead to low re-condensation rates. We consider that it is useful and constructive that theoretical findings by Saleh et al. (2011) are tested and confirmed in other studies. Particularly, in the present work we aim to independently analyse the significance of different factors, including re-condensation, in affecting the estimation of organic aerosol volatility properties. We will present a more thorough account on the motivations and contribution of our study with regards to previous studies in the revised manuscript.

3) *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.*

We do not agree with this statement. According to Dr. Khlystov, the analysis of thermograms (i.e. MFR) applied in our study, and by extension, in all studies based on this approach (e.g., Faulhaber et al., (2009), Cappa and Jiménez, (2010), Cappa and Wilson (2011)) is "problematic" for deriving the volatility distribution of organic aerosols. The analysis of thermograms would be incorrect only in the case that MFR observations were directly used as an indication of volatility, for instance, by directly comparing MFR values at constant temperature (i.e. the lower the MFR, the higher the aerosol volatility), or T50 values at constant MFR. Such an analysis would be misleading because thermograms depend on the initial aerosol mass loading. For a correct interpretation, thermograms must be analysed with the aid of methods that account for the influence of the initial aerosol mass loading, as it is done in our study. For instance, the theoretical calibration curve derived in our study and the kinetic model are explicitly defined as a function of the aerosol mass loading. The analysis of the gas phase mass change (ΔC) suggested by Dr. Khlystov, may well be an alternative method for deriving volatility information, however using ΔC or MFR should be equivalent, as ΔC can simply be derived from MFR and the initial aerosol loading. We agree that if we are to infer volatility information just from direct observation of measurements, the only correct approach would be comparing ΔC values; however, it is shown in the present study and elsewhere, that the combination of MFR measurements with an analysis method accounting for the initial aerosol loading is an alternative methodology that is equally valid. The validity of our approach is supported by previous literature making use of these methods (eg. Faulhaber et al. (2009), Cappa and Jimenez (2010)) and comparison with volatility information inferred from other studies (eg. Figures 14-16 in our manuscript).

4) *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 study does not deal with any analysis on equilibration time, hence a discussion on this area is out of the scope of our work. Even so, we summarised findings on equilibration time estimations by Riipinen et al. (2010) and Saleh et al. (2011) in the introduction of the manuscript. The equilibration time study in Saleh et al., (2011) has not been discussed further in our manuscript because this is irrelevant to our study on re-condensation or volatility estimations. As explained above, we do not consider that we have used “problematic constructs” when employing thermograms in our work. Volatility properties can be derived from particle phase mass change data with the aid of methods that account for the effect of the initial aerosol mass loading (please see arguments in response **3)**.

5) *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.*

We strongly disagree with this statement. We have conducted an extensive parametric analysis on re-condensation, covering all aerosol parameters in a broad and significant range of values. It can be easily seen that our parametric study covers all the aerosol parameters comprised in the dimensionless Cn number by Saleh et al. (2011) (i.e. Np (COA), dp, F(α)). We have explored the effect of aerosol mass loading with values ranging from atmospheric to laboratory levels (30 μg/m3, 50 μg/m3, 150 μg/m3, 400 μg/m3), accommodation coefficients from 1 down to low values leading to negligible re-condensation (1, 0.1, 0.01), average particle sizes typical in thermodenuder experiments (100 nm, 200 nm) and up to 4 orders of magnitude in volatility composition (0.01 μg/m3, 0.1 μg/m3, 1 μg/m3, 10 μg/m3). Furthermore, we have not only tested re-condensation on a parametric analysis, but also reproduced thermograms for single and multicomponent aerosol compositions representative of lubricating oil, succinic acid and α -pinene SOA, in simulations with 2 real thermodenuder designs (Huffman et al. (2008), Grieshop et al. (2009)), plus our parametric analysis TD design (which only differs on the cooling section diameter from Huffman et al. (2008) TD). Therefore, the parametric analysis presented in this work is wide enough to provide insights on the importance of re-condensation in typical thermodenuder experiments. We should note that we do not make general claims in our manuscript that re-condensation is always important for every TD design or conditions, but rather we clearly state that the degree of re-condensation depends on the specific conditions of the experiment (eg. see abstract, L5) and that caution should be taken, as re-condensation may not always be negligible.

As mentioned in response **1)** we have done new calculations with an equilibrium wall condensation boundary condition in order to also account for a lower estimate of re-condensation. Although we have obtained a less significant degree of re-condensation than previously, this is still substantial at high aerosol loadings. In order to test whether the geometry or conditions in our model was above the range of negligible re-condensation defined by Saleh et al. (2011), we have calculated Cn values for our analysis. According to the formulations presented in Saleh et al. (2011), the value of Cn in our parametric study is 2.7-10 for a mass loading of 400 μg/m3 (C*=0.01 μg/m3 and dp0=100 nm). This value is well above the maximum Cn number defined by Saleh et al. (2011), for negligible re-condensation (Cn=0.7), explaining the significant re-condensation levels obtained with our model. Hence, there is no disagreement between our results and those in Saleh et al. (2011). For this Cn value, our model yields 80% re-condensation fraction, while Saleh et al. (2011) predicts a maximum re-condensation of 50%. Although there is still a difference of 30% between our estimations, this may be due to the fact that our model presents radial resolution, while Saleh et al. (2011) solved a one dimension flow model that may not be as accurate to predict local condensation at the walls. In our study we have worked with geometries and conditions representative of some currently used TD designs, such as Huffman et al. (2009), which present Cn values higher than 0.7 at high aerosol loadings (eg. Cn=2-7.4 for 100 nm particles at 400 μg/m3 and C*=0.01 μg/m3). Although Saleh et al. (2011) claimed that the dimensionless number Cn will have a value below 0.7 for the "vast majority" of thermodenuder geometries and experiments, we find that some current TD designs present Cn values above this limit for high aerosol loadings. Whilst we acknowledge that TD geometries can be modified to reduce the effect of re-condensation, the aim of our study is to analyse the problems derived when using currently used TD systems, even if their geometries are not optimum to minimise re-condensation issues. We will add this discussion to the revised version of the manuscript.

Specific comments:

6) *6726/2: In Saleh et al. (2008), equilibrium is not "assumed", it is experimentally verified.*

This sentence states that the method presented by Saleh (2008) to derive thermodynamic properties is based on the assumption of equilibrium, i.e., that this method can be used only under equilibrium conditions. While Saleh et al. (2008) verified this method experimentally, our statement does not relate to any measurements; therefore we do not feel that this text should be modified.

7) *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).*

We disagree with this statement. Riipinen et al. (2010) is based on a modelling study that revealed the dependences of the equilibration time on factors such as aerosol mass loading, volatility and evaporation coefficient. We consider that their study is therefore based on a theoretical analysis.

8) *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.*

We disagree on this point. Although the characteristic equilibration time is not explicitly dependent on the saturation concentration, as shown in the dimensionless analysis by Saleh et al. (2011), the equilibration time is ultimately dependent on the saturation concentration through the dependence of particle size on volatility. The equilibration time is independent of the volatility “under the assumption that the change in particle size upon evaporation is small” (page 578, Saleh et al. 2011). A change in the particle size is, however, inherent to the evaporation process itself; hence, deviation from the above assumption is expected in most practical cases. This can clearly be verified in Figure 6 of Saleh et al. (2011), which shows that the equilibration time increases with increasing volatility. Hence, we do not consider that it is rigorous to state that the equilibration time is not dependent on the compounds volatility.

9) *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 semivolatile organic aerosols from phase equilibration kinetics in a thermodenuder. Aerosol Sci. Technol., 46, 22-30.*

The reference suggested will be included in the text.

10) *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).*

It will be added to the manuscript that Saleh et al. (2011) provides modelling calculations along with experimental results. It is out of the scope of our work to provide a detailed description of each of these models in the introduction to the paper. Only the main differences between the approaches and findings of the models will be summarised in the introduction.

11) *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.*

Please see response **(1)**

12) *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.*

We have probably not described this boundary condition with enough detail in the text. This equation implies that there is no heat transfer between the system and the surroundings in the heating section and that any heat transfer occurs between the walls and the circulating air. In the cooling section the temperature at the walls is set equal to ambient temperature and heat transfer occurs between the internal air flow and the walls. This is clarified in the revised manuscript.

13) *6733: I do not agree that a plug flow profile is a better approximation than the parabolic profile. 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.*

We did not state in the text that a plug flow velocity profile is a better approximation than a parabolic profile, but rather that our calculations showed that the plug flow velocity profile provides a better approximation of the particle evaporation/re-condensation rate for the constant particle concentration radial profile employed in our model. As described in the text, we did not employ a realistic radial profile for the particle concentration, but a constant particle concentration profile (i.e. equivalent to a plug flow distribution). A real particle concentration radial profile would have a sort of "parabolic" shape, with near-zero particle concentration in the vicinity of the walls (due to diffusion and thermophoretic losses) and a maximum particle concentration at the centerline (Shimada et al., 1993). The gas production near the walls of the heating section would be low in a real system, because there would be few particles at this region. The constant particle concentration profile that we use, however, implies having a high particle concentration near the walls, which together with the long residence time defined by the parabolic velocity profile at the walls (velocity ->0), leads to an overestimation of the gas production in this zone. We should clarify that this happens not just at the bin adjacent to the wall, but in the region within ~20% radial distance from the wall where velocities are low. The overestimated production of gas near the walls in the heating section leads to diffusion of gas towards the centerline, thus reducing the evaporation rate of particles at other radial positions. Similar artefact occurs in the cooling section, due to an overestimation of the particle re-condensation rate in the vicinity of the walls. Our comparison with experimental results show that, in the absence of a model for the particle concentration radial distribution, the combination of a plug flow velocity and plug flow particle concentration profiles provides a better approximation for the averaged particle evaporation/re-condensation rates than using the velocity parabolic profile with a constant particle concentration radial profile. We will clarify this issue in the revised manuscript.

14) *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.*

It will be clarified in the text that our definition of RF differs from that in Saleh et al. (2011).

15) *Section 4 and further: All calculations need to be redone with the correct boundary conditions and conclusions re-evaluated.*

Please see response **(1).**

16) *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.*

As mentioned above, we do not address the equilibration time analysis in our work, thus we do not feel it is necessary to describe in detail previous studies on this area.

17) *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.*

We agree that the accommodation coefficient derived by Riipinen et al. (2006) was for an aqueous solution, while in Saleh et al. (2011) the particles were dry, therefore these values are not directly comparable. It should be noted, though, that experiments by Faulhaber et al. (2009) were conducted with dry particles; however, the best fit for the accommodation coefficient was a value of 1, in contrast with the value <=0.1 found in Saleh et al. (2011). The value of Csat used for the calculations was 3.57 μg/m3. This is the averaged value from data provided by Chattopadhyay and Ziemann, (2005), Bilde et al. (2003) and Davies and Thomas (1960). A table with the original values is summarised in Chattopadhyay and Ziemann (2005). Chattopadhyay and Ziemann (2005) and Bilde et al. (2003) employed a TPTD and a TDMA method, respectively, in which the accommodation coefficient was assumed to be 1. This assumption has been shown to be of low significance in TDMA studies, with variations of the accommodation coefficient in a range between 0.2 and 1 leading to less than 30% change in the vapor pressure estimations (Bilde et al. (2003)). In the work of Davies and Thomas (1960) the vapor pressure was determined by means of an effusion method, without any assumption on the value of the evaporation coefficient. The value derived from Davies and Thomas (1960) is in fact very similar to that from Bilde et al. (2003) (P25 of 4.23e-5 and 4.6e-5 Pa, respectively). Thus, it is not evident that the accommodation coefficient value derived in our work was pre-determined by the vapour pressure values used as input to the model. We believe, however, that further work is necessary in order to clarify differences between the accommodation coefficients from different studies. We will add this discussion to the revised manuscript.

18) *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).*

Dr. Khlystov misinterprets that our discussion on re-condensation and residence time in the cooling section is referred to the model analysis presented in Saleh et al. (2011). The discussion presented in our paper focuses exclusively on the experimental results presented in Saleh et al. (2011). Our modelling analysis shows that experiments by Saleh et al. (2011) are not convincing enough to validate their re-condensation theoretical analysis. As Dr. Khlystov points out, because walls condensation was not included in our model it would be expected to obtain significant particle re-condendation when reproducing the experiments in Saleh et al. (2011) with our model. However, even at such favourable conditions for re-condensation, we obtained negligible particle growth, which is attributable to the short residence time in these experiments and the low accommodation coefficient of the aerosol under study. This result, along with our previous parametric analysis led us to conclude that experimental findings of negligible re-condensation in Saleh et al. (2011) were specific to the experimental conditions chosen by the authors and not valid to be extrapolated to other experiments and residence times. Regarding the modelling analysis in Saleh et al. (2011), we do not agree with their claims that the coupling dimensionless number Cn, defined as the ratio between the particles and the walls re-condensation rate, is less than 0.7 for the "vast majority" of thermodenuder experiments and geometries, implying a maximum recondensation fractions of 10%. We find that some of current TD designs present Cn values above this limit for high aerosol loadings (eg. Huffman et al. (2009), Grieshop et al. (2009)) and that re-condensation in these systems is expected to be substantial. Whilst we acknowledge that TD geometries can be modified to reduce the effect of re-condensation, the aim of our study is to analyse the problems derived when using currently used TD systems, even if their geometries are not optimum to minimise re-condensation issues.

We do not make general claims in our manuscript that re-condensation is always important for every TD design or conditions, but rather we clearly state that the degree of re-condensation depends on the specific conditions of the experiment (eg. line 5 in abstract) and that caution should be taken, as re-condensation may not always be negligible. Regarding the last phrase in this comment: yes, the cooling section of the thermodenuder design in our parametric analysis had a diameter of 2.2 cm instead of 1.9 cm; however, the analysis on re-condensation in section 5 was done exactly on the same geometry and conditions as in Huffman et al. (2008) and Grieshop et al. (2009) TD designs. Discussions on these issues are added to the revised manuscript.

19) *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.*

We don't see any conflict between our denuder section calculations and what is pointed out in this comment. Our study agrees with Saleh et al. (2011) that the charcoal denuder is not effective under the assumption of wall equilibrium conditions and that evaporation of the particles may be induced by the denuder. We agree that this is an undesirable effect and we have mentioned this previously in our paper (eg. see abstract). However, we have also shown in our calculations that evaporation is likely to be significant only at thermodenuder temperatures below 40C when the fraction of material with Csat> 1 µg/m3 is significant, and not for all working conditions, as Saleh et al. (2011) study seems to suggest.

20) *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.*

Although we have included the Kelvin term in the initial definition of these equations it should be noted that the sensitivity analysis on the curvature term included in page 6746 (L15) shows that this term can be neglected and that the equilibrium assumption is valid. Subsequent calculations with the equilibrium formulas were in fact done after dropping the Kelvin term from the equations (Figures 10, 11 and 12). This will be clarified in the manuscript.

20) *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".

Equation numbering will be checked, the sign of Delta Cp,i will be corrected and "functional groups" will be replaced by "homologous groups".

21) *R-6748/5-10: the expression derived in the current manuscript for pure components could be more accurate than that in Faulhaber 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.*

This comment is confusing. We cannot clearly identify the formula in Saleh et al. (2008) cited here. If this is equation 6 in the cited paper, we find that this expression has the same temperature dependence as our equation, so we can not see any advantage in using this formula.

22) *6748/11: Saleh et al. (2011) also shows that it is impossible to equilibrate aerosol in ambient concentrations.*

We will add to the paper that Saleh et al. (2011) also shows that it is not possible for the aerosol to equilibrate in thermodenuder measurements at ambient concentrations.

23) *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.*

This comment refers to our statement that equilibrium thermograms from different thermodenuders should be identical if the same initial aerosol loading is employed. We should note that this statement is based on the assumption that thermograms are not modified after leaving the heating section (i.e. on the assumption of negligible re-condensation). Because the Kelvin term can be neglected, the equilibrium equation (Eq. 21) implies that *equilibrium* thermograms for a given aerosol sample are exclusively dependent on the initial aerosol loading. This means that identical thermograms should be obtained regardless of the thermodenuder design, as long as equilibrium is attained and the same aerosol sample and initial mass loading are used. This is because once equilibrium is attained, the particle mass (and by extension, the gas phase mass) remains constant, thus, *equilibrium thermograms* are independent of the residence time or geometry of the system. We therefore do not agree with Dr. Khlystov's statement that equilibrium thermograms defined with equation 21 depend on the heating section design. The degree of particle evaporation (i.e. MFR) depends on the heating section residence time only when equilibrium is not attained. We will clarify that this statement applies to conditions in which re-condensation is negligible (i.e. thermograms are not modified after leaving the heating section) in the revised manuscript.

Unfortunately, Dr. Khlystov did not take enough time to read the text accompanying the description of equation 25 and its application in this study in combination with equations 23 and 24. We present this equation not to infer any information from thermodenuder measurements, as Dr. Khlystov seems to believe, but to illustrate the change in the aerosol mass due to dilution or cooling under equilibrium and kinetically-controlled conditions for organic aerosols of known composition (Figure 13). Hence, objections to the use of this equation for deriving information from thermodenuder measurements just do not apply to what is explained and presented in our study.

24) *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.*

In this comment, the purpose of the calculations presented in Figure 13 is misinterpreted. These calculations do not intend to provide a realistic detailed model estimation of the aerosol mass variations in the atmosphere, in which the change of the initial mass loading should be accounted for, as Dr. Khlystov seems to believe. These calculations are presented to illustrate the difference in estimating the aerosol mass modification upon temperature and dilution ratio changes, when assuming equilibrium or kinetically-controlled conditions, not to model particular atmospheric complex phenomena. For comparison purposes, the calculations are normalised with respect to the initial aerosol mass loading. We will suppress that the model represents convective lifting and will clarify in the text that these calculations have been included with an illustrative purpose and not to provide an accurate modelling estimation in which aerosol mass changes should be accounted for.

25) *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.*

The equilibrium formulas were not used to estimate the non-equilibrium conditions, as Dr. Khlystov believes. It was the kinetic model that was employed for the non-equilibrium conditions calculations. This will be clarified in the text of the revised manuscript.

26) *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?*

The presented model has initially been designed to simulate the behaviour of monodisperse aerosol samples. An extension of the model would be required so that it can be used to represent polydisperse distributions. This can be done by implementing approaches such as the condensation sink diameter (Saleh et al., 2011), which is the particle diameter of a monodisperse aerosol that exhibits the same net evaporation or condensation rate as a polydisperse aerosol. A detailed description of this method and its implementation on a kinetic evaporation model can be found in Saleh et al. (2011).

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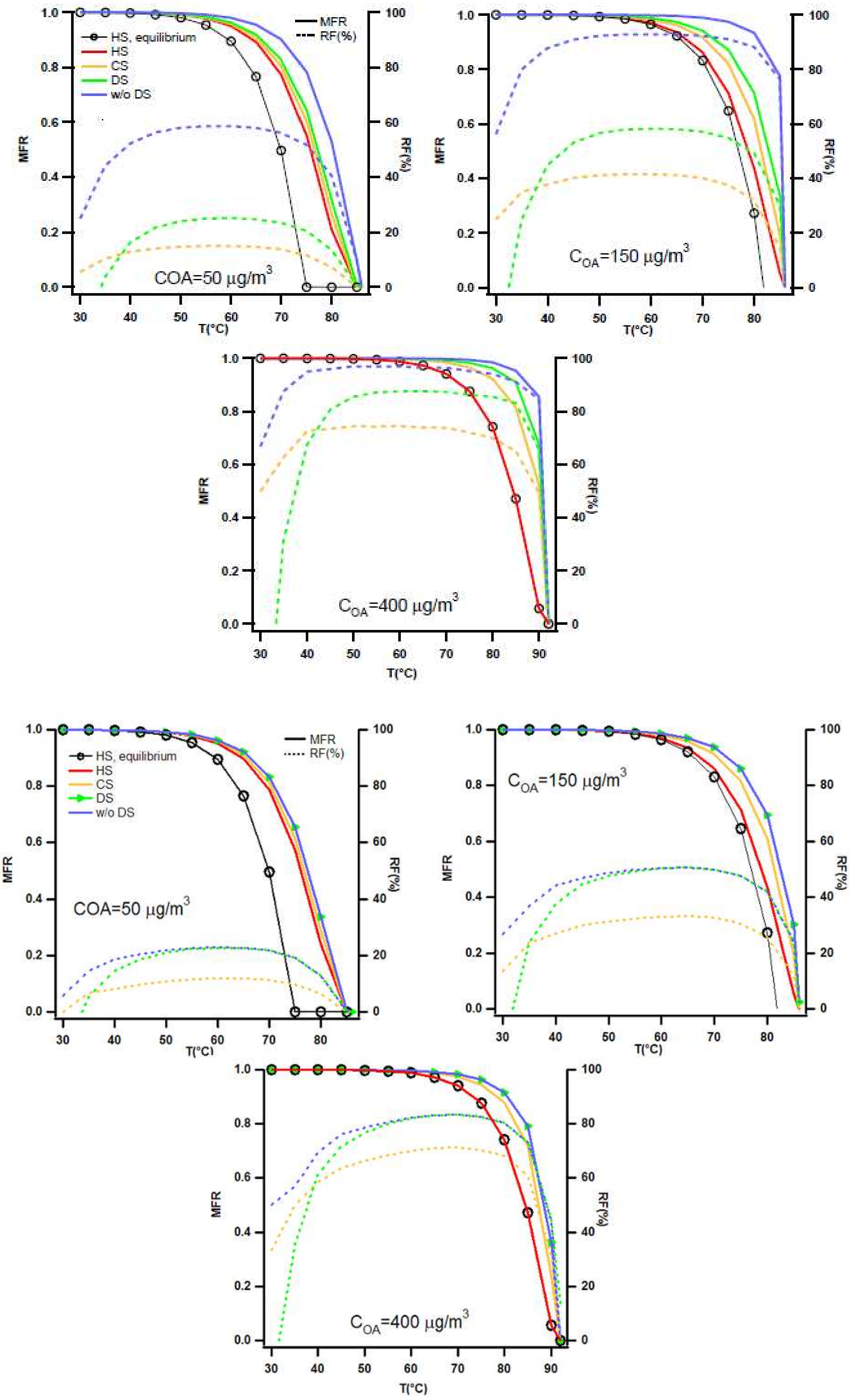

Figure **R1**: Upper (top 3 figures) and lower (bottom 3 figures) estimates of re-condensation as a function of aerosol mass loading. Plots represent output thermograms (MFR) and re-condensation fraction (RF) for the heating section (HS), cooling section (CS), denuder section (DS) and equivalent configuration without denuder section (w/o DS). Baseline case: *C*sat =0.01 μgm−3, *d*p =100 nm, D*i*=5×10^{-6} m^2/s and *α*=1.

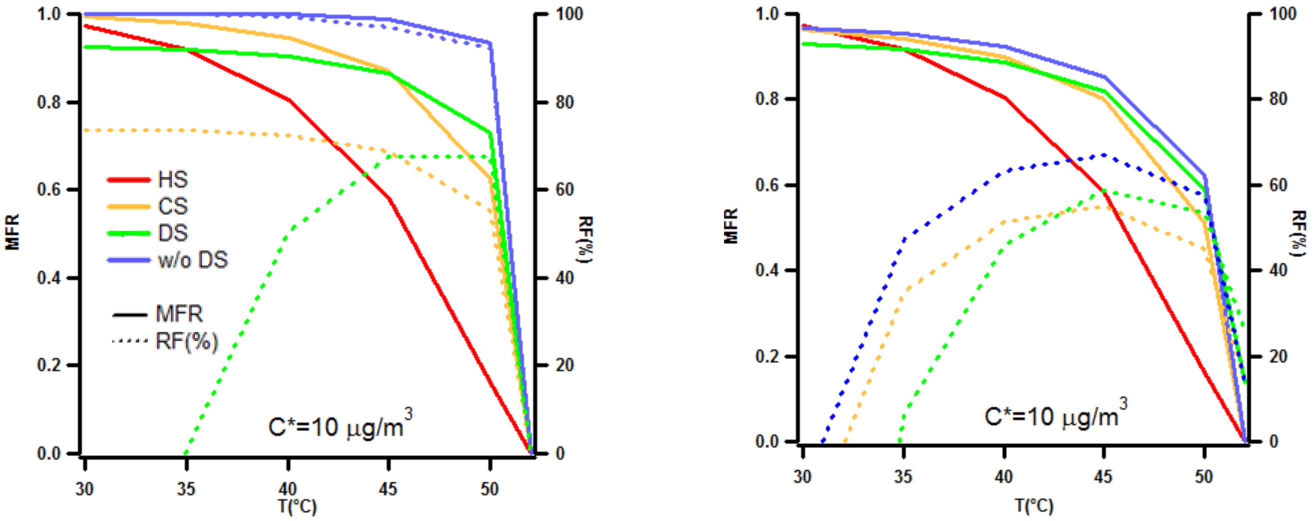

Figure **R2**: Upper (left) and lower (right) estimates of re-condensation for the case with Csat=10 µgm−3, C_{OA}=400 µg/m3, *d*p =100 nm, D*i*=5×10^{-6} m^2/s and *a*=1. Plots represent thermograms and re-condensation fraction for the heating section (HS), cooling section (CS), denuder section (DS) and equivalent configuration without denuder section (w/o DS) .