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***Interactive comment on “Measurement of the ambient organic aerosol volatility distribution: application during the Finokalia Aerosol Measurement Experiment (FAME-2008)” by B. H. Lee et al.***

**B. H. Lee et al.**

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1. *Lee et al. present measurements from the FAME2008 campaign of ambient OA mass loadings and how the OA mass changes as the particles are passed through a thermodenuder (TD) maintained at elevated temperatures. An interesting contribution from this paper is the measurement of mass thermograms for different TD residence times (14 sec and 105 sec). Their results clearly indicate that the particles do not achieve equilibrium in the TD within 14 seconds, indicating that a non equilibrium model must be used to interpret the observations. However, only a few data points at the*

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*longer residence time were measured, which, in my opinion, limits the consideration of these longer residence time results to be qualitative. My overall opinion is that the conclusions are not completely justified by the presented analysis and tend to overstate the case that can actually be made in many places. As with Reviewer 1, I believe that significant revisions to this manuscript will be necessary before it can be considered for publication. However, I do think that ACP could be an appropriate venue despite the relatively heavy “technical” side to the paper, so long as revisions are made to emphasize and clarify the “science”.*

The valid issues raised by the referee here are also addressed in our responses to the comments 8 and 9 of Referee 1. In summary, the OA AMS spectrum and properties were surprisingly constant during the whole month of measurements. The three data points in Figure 8 actually correspond to three different days and roughly 30 hours of measurements. We have repeated the analysis using two more approaches (please see our reply to Comment 15) and shown that our conclusions remain valid no matter how the points at different residence times are treated. While it is clear that more measurements are needed in different residence times during similar field studies, we think that our results are robust given the observed constant state of the very aged OA during FAME-08. This important issue is discussed in the revised paper.

**2.** *The vast majority of the measurements were made over a very limited temperature range (ca. 100 to 115 C). The authors should explicitly comment on why such a limited temperature range was considered. Other recent ambient TD/AMS measurements have generally taken the approach of using temperature ramps in order to allow for measurement of mass thermograms with data points that span a much larger temperature range. The temperature ramp method effectively provides greater information content than when a narrow temperature range is considered, as was done here.*

This is another valid point also raised in the Comment 8 of Referee 1. Our study was designed to investigate the changes in volatility as a result of the change in OA compo-

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sition and source region. Therefore most of the measurements were taken at around 110 C. The surprising result of the study was that the AMS OA spectrum showed very little variability during the whole month of the FAME-08 study (Hildebrandt et al., 2010). While this could be seen as an advantage because it allows us to analyze our measurements together, it resulted in a sub-optimal distribution of measurements (too many of them at the same residence time and temperature and fewer in the rest of the space). Despite this, given the little variability of the investigated OA and its volatility and the fact that each data point in Figure 7 represents an average of approximately 20 hours of measurements we think that our results are robust.

**3. p. 17442:** *The authors put forth a correction scheme that can be used to determine changes in particle collection efficiency in the AMS upon heating of the particles. They state that the CE is 85 percent for ambient particles but that this decreases to 76 percent for denuded particles (it is not stated at what temperature this was determined). Following this, they state that “After application of this collection efficiency, the AMS sulfate concentration agreed well ( $R^2 = 0.95$ ) with concentrations measured independently by PM1.3 filters (Hildebrandt et al., 2010) during the full duration of the study. This agreement increases our confidence in the estimated CE values.” It seems only fair to also mention that the same comparison was done for OA by Hildebrandt et al., with a somewhat lower  $R^2$  value (0.78), although it is possible that some of the additional scatter in the OA arises. It should also be made clear that it is only the ambient, and not the denuded, measurements where the AMS mass was compared with filter based measurements. As such, I do not see how this comparison provides confidence in the results for the derived thermodenuded CE. Finally, can the authors comment further on the comparison between the AMS and filter results given that the filter results were for PM1.3 while the AMS is only sensitive to particles less than 1 micrometer?*

There are several points here. First we agree with the reviewer that the agreement between the filter-based concentrations of sulphate and the AMS derived ones increases our confidence on the estimated CE values for the ambient particles. We do not have

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independent supporting evidence for the estimated CE of the thermodenuded aerosol. This is now clarified in the revised paper.

The second point concerns the difference in the cut-point between the AMS and the filter-based measurement. This is in general a small fraction of the PM<sub>1</sub> mass and in similar environments is dominated by NaCl, NaNO<sub>3</sub>, etc. The sulphate and OA concentrations in this 1-1.3 micrometers region is usually much less than 10 percent of the PM<sub>1</sub> sulfate and OA in Finokalia (Gerasopoulos et al., 2007). This point and the corresponding reference have been added to the revised paper.

Gerasopoulos, E., E. Koulouri, N. Kalivitis, G. Kouvarakis, S. Saarikoski, T. Mäkelä, R. Hillamo, and Mihalopoulos, Size-segregated mass distributions of aerosols over Eastern Mediterranean: seasonal variability and comparison with AERONET columnar size-distributions, Atmos. Chem. Phys., SRef-ID: 1680-7324/acp/2007-7-2551.

**4.** *p. 17442 and Figure 2: Since an AMS was used behind the TD the authors were also able to measure sulfate concentrations. Was there any loss of sulfate through the thermodenuder (i.e. did the MFR for sulfate decrease below 1)? If so, can the authors comment as to what extent this might have influenced the collection efficiency? In other words, is it possible that the deduced changes in CE resulted from changes in sulfate and not organics alone?*

There was some evaporation of ammonium bisulfate and ammonium sulphate at the relatively low temperatures (100-140 C) used in our measurements because of the relatively high residence times used (14-105 s). The evaporated fraction of sulphate was small for most measurements (less than 10 percent) which were at 110 C and was also accompanied by evaporation of ammonium and water. It is not clear what caused the change in the CE so the best that we can offer is a series of hypotheses. The loss of the more volatile organics is one of them. The loss of aerosol water is another potential explanation. There could also be morphology changes (e.g., “melting” of the organics if they were originally in a glass-like state) that changed the behavior of

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particles in the TD. We cannot eliminate the possibility that the evaporation of sulphate also contributed in some not-yet-understood way to these changes. Our main point here is that the assumption of a constant AMS CE when the AMS is coupled to a thermodenuder may not be always a valid assumption. Obviously this issue requires further investigation in future studies. We have added the summary of the discussion above to the revised paper.

**5.** *p. 17442 and Figure 2: Can the authors comment more specifically on the difference between the CE values determined for this study and the typically assumed value of 0.5 (see Canagaratna et al., 2007), especially given that the particle mass was dominated by sulfate? At minimum, a reference to Hildebrandt et al. (2010) seems necessary since this is discussed to some extent in that paper.*

One potential explanation (also mentioned in our Hildebrandt et al. paper) is that in this study the sulphate was almost always in the form of ammonium bisulphate and did not effloresce even at low RH. This may have reduced the bounce of particles in the AMS. There are other potential explanations including the specifics of the Q-AMS used in the study. While the typically assumed values are reasonable guesses when no other information is available, it is becoming clear that independent estimation (or at least confirmation) of the CE used is required. Otherwise, the estimated absolute concentrations are accompanied by considerable uncertainty. We believe that the approach used in our study (the SMPS and AMS distribution matching) can contribute to this effort. Filter- or steam-sampler-based measurements are also very useful. A brief discussion and another reference to the Hildebrandt et al. (2010) paper have been added.

**6.** *p. 17442: At what temperature was the average density for the denuded particles determined? I assume 110°C, although measurements were made up to 140°C?*

The average density is for all measurements. The density of the OA remaining after

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evaporation at 110 C ( $1.26 \pm 0.24 \text{ g cm}^{-3}$ ) was not statistically different from that of the OA remaining at 140 C ( $1.31 \pm 0.31 \text{ g cm}^{-3}$ ). This point has been clarified in the text.

7. p. 17443: *The authors state that the CE results are relatively insensitive to their treatment of particle water. However, I would assume that most of the water is removed from the denuded particles prior to measurement in the AMS. As such, the denuded and ambient particles may have very different water contents. It is stated that if it is assumed that the particles lose half their water in the AMS inlet then the CE changes by less than 5 percent. However, if the ambient particles contain water but the denuded particles have no water then the same assumption as to particle water should not be made for the denuded and ambient particles. How would this affect the CE results? Can I assume that if loss of half the water leads to a 5 percent change in the estimated CE then loss of all the water would lead to a 10 percent change? A change in the thermodenuded CE by 10 percent would be large enough to bring it into agreement with the nondenuded CE. However, related to this, if particle phase water is indeed removed in the TD (which I believe it would be), wouldn't one expect the decrease in CE to be greater than was observed since it was argued in Hildebrandt et al. (2010) that the reason for the "high" collection efficiency ("high" meaning  $> 0.5$ ; Canagaratna et al., 2007) was that the particles contained enough water so as to be liquid? Also, since it is stated that particle water ranged from 0 to 20 percent, shouldn't periods of low CE have been observed when low particle water was observed?*

This is an excellent point related to the potential differences in water of the particles detected by the AMS and the SMPS. Please note that the AMS water was used in the CE collection algorithm both for the ambient and thermodenuded measurements. This water was practically zero for the thermodenuded aerosol. So this effect was taken into account in our CE calculations. The potential problem concerns potential differences between the water in the particles measured by the SMPS and the AMS. We have recently published additional relevant findings in Engelhart et al. (ACPD, 2010) where we report that the water estimated from the AMS measurements (assuming relative ion-

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ization efficiency equal to 1) is consistent with the actual water content of the particles (that was measured by the AMS). This suggests that there are no major problems in our CE estimate related to the way that water and its evaporation in the TD was treated. Our sensitivity study is a worse case scenario of a factor of 2 error in the above analysis. So the 5 percent error in the CE is the worst case for this effect. A higher error is completely inconsistent with the Engelhart et al. (2010) results. This rather complex issue is discussed in more detail using our most recent findings in the revised paper.

**8.** *p. 17443: I find the discussion of the particle number loss to be insufficient with respect to the treatment of temperature dependent losses. The authors report only one value for the particle loss through the TD (15 percent), but do not report the temperature to which this corresponds. They state that the fractional loss is temperature dependent, but do not state how they account for this temperature dependence. Since they do not show a figure they must at minimum report the equation that they use to determine the temperature dependent losses. Furthermore, it appears that this loss rate was determined by plotting the particle number concentration from the TD vs. ambient and determining the slope (Figure 3). Implicit in this methodology is the assumption that the particles are internally mixed. If the particles were externally mixed to any extent then it is entirely possible that some particles could evaporate entirely whereas others will persist in the TD. This implicit assumption should be stated and, if the data exists (such as can be obtained from single particle measurements), justified by observations. If some particles do evaporate entirely as they transit the TD, they are removed from the distribution, but this is not really a “loss” in the sense that it is used here. As such, the 15 percent would seem to be an upper limit. What was the loss at the high residence time?*

Our presentation of this loss analysis was probably confusing and has been revised. The 15 percent was the average particle loss during the study. This is given to inform the readers about the magnitude of the losses in this TD for the conditions of the study. All the data points (24 min averages) are presented in Figure 3. The losses at the

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higher temperatures were higher (a little more than 20 percent on average). We did not use the average loss (15 percent) for the correction but as we stated in the end of section 2.2.2 “we assume that a size-independent correction factor that is determined for each sample (every 24 min) is sufficient for this dataset.” So for the higher temperature measurements we used the corresponding loss correction determined for that sample by switching between the thermodenuded and the bypass line.

We agree with the reviewer that our methodology implicitly assumes that the particles are internally mixed. This assumption is supported by the lack of local sources affecting the site during FAME-08 (Hildebrandt et al., 2010; Pikridas et al., 2010), the lack of particles smaller than approximately 50 nm during the periods without nucleation (Pikridas et al., 2010), and the significant residence time of particles in the atmosphere (more than a day during most of the study) before reaching the site. All of these suggest that the particles in this site (as in most remote sites) were quite close to the internally mixed state. We do state now this assumption explicitly and also present the above arguments supporting them.

Our consistency check for both the number and volume distributions (Figures 4 and 5) is addressing, among other issues, the concern of the referee that our number-based correction is affected by complete evaporation of particles. If this was a significant problem there would be significant discrepancies in the measured and estimated size distributions. This is clearly not the case. Once more, this issue does deserve some additional discussion that has been added to the paper.

**9. p. 17444: Algorithm Consistency Check:** *It is not clear that this is indeed a “consistency” check. The CE and density values were determined based on a comparison between AMS and SMPS data and thus the results for one are not separable from the results of the other. As such, the results shown in Figures 4 and 5 do not seem to provide added confidence that the corrections are reasonable, only that that they were applied correctly. Similarly, the check provided in this section does not support*

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*the claim that the AMS and SMPS are consistent with each other. In fact, given that the AMS results were corrected using the SMPS results it would be surprising if the corrected values were not in agreement!*

The value of this test and therefore the consistency of our approach is the result of matching the complete number and volume size distributions. A number of assumptions are used in the analysis and if any of them were problematic our results would not pass this test. The referee has already mentioned two of them in Comment 8 (the internal mixing assumption and the potential complete evaporation of some particles). If these assumptions were problematic either the mass or number distributions would not match. Other assumptions include the size-independent loss corrections, the size-independent collection efficiency for both the ambient and thermodenuded aerosols, etc.

We should also underline the importance of matching the number distributions even if the CE was calculated from the mass/volume distributions that are practically zero in at least half the size range covered by the number distributions (Figure 5). Also the importance of matching the mass distributions with the loss correction estimated from the number distribution. These do increase our confidence in the consistency of our measurements and of course on the fact that everything was done correctly.

Our claim regarding the consistency of the AMS and SMPS results from our ability to reproduce accurately the full SMPS number and volume distribution from the AMS-calculated evaporated fractions and composition and one parameter (the CE). This does show some level of consistency between the two instruments once more considering the full distribution functions.

So the test is indeed valuable and is highly recommended for similar studies to test the underlying assumptions.

**10.** *p. 17446: I believe that the continued references to the unpublished Lee et al.*

*paper are not warranted given that this paper is not yet published. References to this unpublished manuscript should be minimized and the reference should be given as a footnote to make it clearer to the reader that they are referencing unpublished work.*

This is a valid concern. We have replaced this reference with one to the PhD thesis of Lee that is currently available.

**11.** *p. 17446: The authors have selected as a base case to use  $\Delta H_{\text{vap}} = 80$  kJ/mol, which they state is “not far from the Saathoff et al. (2009) estimate for the less volatile alpha pinene SOA component.” However, Saathoff et al. actually report a value of 59 kJ/mol. It has been shown (Cappa, 2010) that TD models are particularly sensitive to the choice of  $\Delta H_{\text{vap}}$  for  $\Delta H_{\text{vap}}$  values of less than 100 kJ/mol, and therefore the difference of 21 kJ/mol between the base case here and the Saathoff et al. results could actually be considered as quite different, rather than “not far from.”*

We have deleted this sentence to avoid the subjective meaning of “not far”. A range of enthalpies starting from 45 kJ/mol is used in our sensitivity analysis covering the Saathoff et al. (2009) reported values.

**12.** *p. 17446: A reference to Saleh et al. (2009) should be included. Saleh et al. found that the effective mass accommodation coefficient for a few dicarboxylic acids was less than 1. Also, a reference to Grieshop et al. (2009) is needed, since they (somewhat strangely) found an effective mass accommodation coefficient for lubricating oil was much less than one. Associated with this, it is difficult to ascertain to what extent the 0.05 value for the mass accommodation coefficient is reasonable given that the Lee et al. (2010) paper is not published and that the papers by Grieshop (2007, 2009) suggest a much lower mass accommodation coefficient (0.001 to 0.01). Given the inherent uncertainty in the mass accommodation coefficient, I would argue that a better “base case” would be to use a value of 1 and to use alternate values as “other” cases. This suggestion is further justified by the finding that the data can be equally well fit using*

*a mass accommodation coefficient of 0.05 or 1, just with basis sets that vary over different volatility ranges. Thus, by using a value of 1 as a basecase all other mass accommodation coefficient cases can simply be understood as an equivalent increase in the  $C^*$  values of the bins in the basis set.*

We have added the suggested references reporting lower than unity accommodation coefficients. The reference to Lee et al. (2010) has been replaced by Lee (2010).

We do understand the point of the referee about changing the base-case to that of unity accommodation coefficient. On the other hand the evidence does point to values less than unity so we would prefer to keep the current structure of the paper.

The  $C^*$  values in the basis set refer to the thermodynamics of the system. We would prefer not to mix them with quantities referring to its dynamics (like the accommodation coefficient).

**13.** *Figure 6: It is easily understood why the corrected MFR is greater than the uncorrected MFR. However, it also appears in this figure that the thermodynamic temperature for each point has been shifted with the correction. It is not clear why this should be the case and seems to be a mistake.*

We have redrawn the figure and corrected the small discrepancy in temperatures due to two different versions of the dataset used for the plotting.

**14.** *p. 17448: OA Volatility Distribution: I find the use of three different basis sets to be confusing. It should be equivalent to use a single basis set that ranges from the lowest value,  $0.001 \mu\text{g}/\text{m}^3$ , to the highest value,  $100 \mu\text{g}/\text{m}^3$ , considered. This simply corresponds to having 6 bins instead of 4, with some of the factors set to zero. The use of a greater range of values in the volatility basis set (i.e. more bins) ultimately provides greater flexibility in the model and would (likely) result in the authors being able to fit the data well over a broader range of conditions.*

We have tried this and a number of other approaches to the fitting. The underlying problem is that there a lot of free parameters and a rather simple curve (a monotonically decreasing S-like curve) to be fitted. This results in a lot of solutions to this problem. Our approach has been to reduce the number of free parameters by reducing the number of bins in the basis set or adding artificial constraints (making the mass in the first two bins the same and doing the same for the last two bins). So if anything our problem is that we already too much flexibility.

**15.** *p. 17448: In fitting their observations to the volatility model, the authors chose to give equal weight to the short (14s) and long (105s) residence time measurements, despite the fact that considerably more measurements were made at 14s. To achieve this, they replicated their 105s data to have an equal number of points as the 14s data. I believe that this procedure unfairly weights the 105s data and should not be done. It is my opinion that a more appropriate method would be to first fit one of the data sets (14s) and then to compare the calculated mass thermogram at 105s determined using the fit parameters to the observations. Further, consider that the variability in the 14s observations is fairly large around a given temperature. Therefore, one might ask if the three data points that make up the entirety of the 105s data set are really very robust. For example, the VFR for the single point at 130° C is greater than at 110° C, which is a physically unrealistic result. Therefore, the data fit should only be done on the 14s data or, if the authors insist on including the 105s data in their fit, only the three data points should be included (i.e. there should be no data replication). Related to this is the actual fit to the observations. Visual inspection of Figure 7 suggests that the fit to the data is actually quite poor: the model fails to capture the majority to the data points at 110° C, tending to give higher VFR results than were observed. Shouldn't a best fit to a model generally pass through the region where the majority of the data points are located, which in this case is in the 110° C region? I would guess that this inconsistency is likely a result of including the replicated 105s measurements in the fit (see the above point).*

We have followed the reviewer's suggestion and fitted only the 14 s residence times neglecting the longer residence times. The best fit for the data once more corresponded to the volatility basis set [0.01, 0.1, 1, 10] but with mass fraction values [0.3, 0.2, 0.1, 0.4] instead of the basecase values [0.2, 0.2, 0.3, 0.3]. So use of the short residence time measurements results in an increase of the predicted material with relatively low volatility (less or equal than 0.1 micrograms per cubic meter) from 40 percent to 50 percent of the total.

We also repeated the fitting exercise including the higher residence time results but without increasing their weight. Once more the best fit corresponded to the to the volatility basis set [0.01, 0.1, 1, 10] but with mass fraction values [0.2, 0.2, 0.2, 0.4].

These results suggest that our conclusions about the volatility distribution are relatively robust with respect to the treatment of the short and long residence time points in the optimization. While this treatment does introduce some uncertainty in the calculated volatility distributions, it does not affect our conclusion about the relatively low volatility of the organic PM during FAME-08.

**16.** *p. 17448: OA Volatility Distribution: No reference to the recent work by Cappa and Jimenez (2010) is given in this work. This is a significant oversight given that Cappa and Jimenez used a similar methodology to deduce volatility basis set's for ambient aerosol (from the MILAGRO campaign). A reference to that paper is clearly needed and discussion of the results from this study in terms of the conclusions of that paper should be added. In this context, the statement on page 17438 that a "lack of the corresponding theoretical analysis" makes comparisons between different studies difficult should be revised. Cappa and Jimenez (2010) showed that it is possible to fit field observations to a similar volatility basis set/evaporation model with a number of different assumptions regarding the enthalpy of vaporization. In order to fit the observations it was necessary to adjust the number of bins in the basis set, with more bins generally necessary for higher  $\Delta H_{\text{vap}}$  values. However, the important result was that the obser-*

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*vations could be well matched to the model using many different assumptions as to the  $\Delta H_{vap}$ . The authors should comment on this previous finding in light of their model results, which only briefly investigated the influence of different choices of  $\Delta H_{vap}$  and used a limited number of bins (four) in the basis set.*

We have added the reference to the recent Cappa and Jimenez (2010) paper together with the corresponding discussion. Discussion has also been added about the importance of the  $DH_{vap}$  for the calculation of the volatilities and also the number of bins. Briefly, we do agree about the importance of the generally uncertain  $DH_{vap}$  (which should in principle be different for each volatility bin). We did try to address it spanning a wide range of volatilities (from 45 to 200 kJ/mole in the Epstein et al. (2010) parameterization). We also did explore the sensitivity to the bins used with values ranging from  $10^{-6}$  to  $10^{-3}$  micrograms per cubic meter. We used a different approach than Cappa and Jimenez (2010) for the selection of the bin number and location. However, both approaches in the end rely on only a couple of parameters to determine the volatility distribution. Both studies do conclude that there can be a lot of solutions to the problem but that one can still derive some general conclusions about the order of magnitude of the volatility of the OA.

Our statement on page 17438 is consistent with the conclusions of Cappa and Jimenez (2010); use of just the thermodynamic measurements without the corresponding modelling can lead to erroneous conclusions about the volatility of the OA. This is now explained further in the text.

**17. p. 17448:** *The authors conclude that “the observations can be explained with all the OA being semivolatile ( $C^*$  great or equal than  $10^2 \mu\text{g}/\text{m}^3$ ).” However, their TD measurements only go out to 140 C and thus do not provide firm constraints on the lower limit of the OA volatility. For example, it is possible (at least in theory) for the presented mass thermograms to flatten out at higher temperatures, thus necessitating ever lower volatility compounds. The authors need to be more specific by stating that*

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at least e.g. 60 percent of the OA mass is semivolatile (with the 60 percent figure derived from the minimum MFR for the 14 s results).

We agree that while our conclusion is correct it does need to be qualified given the lack of information about the behaviour of the OA at very high temperatures. We have followed the referee's suggestion and added the corresponding qualifying statements.

**18. P. 17449:** *The authors state that the FAME-2008 aerosol is ca. 2 orders of magnitude less volatile than fresh laboratory generated SOA from alpha pinene ozonolysis. A more precise statement would be that they determined that the FAME-2008 aerosol has some components that are 2 orders of magnitude lower than the lowest volatility components determined for the lab SOA (for the base case). This is different than stating that the aerosol itself is lower volatility by 2 orders of magnitude. However, to return to a previous point, the lowest volatility bin considered here is likely an upper limit, since the MFR measurements only go to  $MFR = 0.4$  (for the 14 sec TD). Also, this is only true for the base case, which assumes a mass accommodation coefficient of 0.05. If the mass accommodation coefficient is assumed to be 1 then the volatility of these "low" volatility components will effectively be decreased and the apparent lab/ambient gap will grow. Further, this conclusion will change if a different value is assumed for the enthalpies of vaporization. If smaller  $\Delta H_{vap}$  values are assumed, the ambient aerosol will appear to be comprised of higher volatility components than if higher  $\Delta H_{vap}$  values are assumed. Thus, I believe that this particular conclusion is fraught with unstated caveats (this is one example of where I find the paper to overstate the case).*

We have tried to make this conclusion a little more precise by stating that most of the OA is two or more orders of magnitude less volatile than the fresh monoterpene SOA studied in the lab. This does account for the uncertainties in the accommodation coefficient and the higher  $\Delta H_{vap}$  values. The possibility of a much lower  $\Delta H_{vap}$  is not consistent with our knowledge of the size and molecular structure of these highly oxygenated organic compounds.

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**19.** *P. 17449: The authors state that assuming a  $\Delta H_{\text{vap}}$  value of 45 kJ/mol does not reproduce the measurements as well as if 80 kJ/mol is used (with an accommodation coefficient of 0.05). However, again I believe the replication of the 105 s observations is driving this result. Looking at the fits in Figure 9, it seems clear that if only the 14s observations were included the 45 kJ/mol assumption could easily be used to give just as good a fit as the 80 kJ/mol assumption.*

We agree that the 45 kJ/mol value with accompanying parameters is consistent with the lower residence time measurements and it deviates from the higher residence time measurements. However, we cannot just forget about these 30 hours of measurements at this higher residence time in this environment characterized by the low variability of the OA. If anything, this stresses the importance of performing measurements at a range of residence times, because it increases our ability to constrain the parameters that we are trying to estimate. We have added a paragraph discussing in more detail different fits of the data including the reviewer's suggestion of changing the weighting between measurements at different residence times.

**20.** *p. 17450: The authors find that it is not possible to fit the model to the observations when enthalpies estimated using an empirical relationship given by Epstein et al. (2010) are used. The difficulties in using this empirical relationship have previously been discussed by Cappa and Jimenez (2010) and arise from the rapidly increasing enthalpies of vaporization with decreasing vapor pressure. Given that one of the authors (Riipinen) was on the Epstein paper, and that the relationship given by Epstein is empirical (and therefore, in some ways, more physically plausible than the fixed 80 kJ/mol base case), further discussion of the problems associated with using the Epstein values seems warranted. It is my guess that the difficulties associated with using the Epstein relationship here are in part related to the discussion given in Cappa and Jimenez and in part related to the fact that a basis set was used that only spans 4 orders of magnitude. It is likely that, given enough bins in the basis set, the authors would be able to ultimately obtain a reasonably good fit to the data. This is an inherent*



*limitation of use a pre-constrained number of bins for the volatility basis set.*

We have tried a number of different choices of bin numbers, locations, etc. and the best fit that we were able to obtain is the one discussed in the paper. While it is always possible with using a large number of parameters one could fit the data, we do find this exercise problematic. The data that we are trying to fit correspond to two monotonically decreasing S-curves. One can imagine a model with three may be four free parameters fitted to these measurements. Anything more complex than that clearly constitutes over-fitting and the results are probably questionable. We do recognize the point of the referee and we now mention in the paper that the best fit using up to 5 free parameters is the one discussed in the test. There are probably much better fits if one uses more free parameters, but their results are not meaningful. This does not say anything about the overall value of that DHvap parameterization, it just concludes that we cannot use it to analyze this specific dataset.

**21.** *p. 17451: The authors suggest that even longer residence times than 105 seconds may be needed to ultimately constrain the volatility of ambient OA from TD measurements. Can they comment on the experimental feasibility of going to such long residence times for field measurements?*

Use of the 105 s residence time is a challenge. Use of even higher residence times will probably require a major redesign of the current TDs. However, we do believe that it will be feasible after the community invests some effort in this direction. This is now mentioned in the text together with the major challenges (space and losses of particles).

**22.** *General: As mentioned by reviewer 1, the assumption that reactions within the TD have not modified the aerosol properties (beyond evaporation, of course) should be stated along with appropriate references (e.g. Denkenberger, 2007).*

This is now clearly stated in the paper together with the corresponding references.

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**23.** *Figure 10: I believe that this figure is unnecessary. The text on p. 17450 is sufficient to make the point, not to mention that the basis set used for the alpha equals 1 case is shifted one order of magnitude down from the alpha equals 0.05 base case.*

We have deleted this figure and added some more text discussing the differences in predicted gas-phase semivolatile organics in the two cases.

**24.** *Figure 8 and 17449: The authors present sample volatility distributions for a total organic concentration of 10  $\mu\text{g}/\text{m}^3$  and for a total aerosol concentration of 2.8  $\mu\text{g}/\text{m}^3$ . It is easy to understand why the 2.8  $\mu\text{g}/\text{m}^3$  value was used (the average for the campaign), but more discussion is necessary in relation to the 10  $\mu\text{g}/\text{m}^3$  case, if it is to remain. I would actually recommend removing the 10  $\mu\text{g}/\text{m}^3$  case as it doesn't seem to add much to the discussion beyond the 2.8  $\mu\text{g}/\text{m}^3$  case (i.e. the distributions don't really look very different).*

The value of the 10  $\mu\text{g}/\text{m}^3$  comparison is to illustrate the other case of these partitioning calculations, that of the same amount of semi-volatile material. This distinction between comparisons at the same aerosol concentrations and at the same total concentrations is not appreciated and often leads to misunderstandings and confusion. We would prefer to keep it because there are significant differences in the absolute values of these two cases.

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