

Response to reviewer comments on “Quantitative Estimates of the Volatility of Ambient Organic Aerosol” by C. D. Cappa and J. L. Jimenez

We thank the reviewers for their comments. Our responses follow below. The reviewer comments are given in regular font below while our responses are italicized and given in blue.

Response to Reviewer #1

R1.1. In the introduction it would be good to present the reader with a brief overview of attempts used to derive what one would call mechanistic frameworks using bottom-up approaches. Whilst not as easily or directly applicable to, let's say, large scale prognostic models, these approaches are attempting to attack the problem from a completely different yet entirely complimentary angle. Whilst a thorough review is clearly outside of the present scope of the paper, the use of adequate references alluding to these approaches would help place the current work within a wider framework.

We have added additional references to studies employing “bottom-up” approaches to determine ambient OA concentrations and physical properties. Additionally, the reader is now referred to the comprehensive review of Hallquist et al. (2009) for further details.

R1.2. Page 1906-1907. In the discussion of enthalpies of vaporization and impacts of variations in C^* , the authors reference studies on individual dicarboxylic acids. Would the authors consider these acids as adequate 'reference' points from which to generalize results? Again, I understand the difficulty here, but it is likely that many readers do not given the relative infancy of this area with regards to atmospheric science.

The semi-empirical relationship between C^ and ΔH_{vap} determined by Epstein et al. is based on a large set of compounds, not only dicarboxylic acids. Unfortunately, the lowest C^* values for the compounds used to determine the semi-empirical relationship does not cover the entire range of C^* values considered in this study. As we note, use of their relationship unmodified leads to the prediction of extremely large (unphysical) ΔH_{vap} values. Thus, we determined it is important to limit the maximum ΔH_{vap} . To move beyond the single reference to the study on dicarboxylic acids*

we have added a reference to Chickos and Acree (2002), which summarizes measurements of ΔH_{vap} for a large variety of organic compounds. Considering compounds only containing C, H and O atoms, the highest ΔH_{vap} value reported in Chickos and Acree (2002) is 198.5 kJ/mol (for $C_{100}H_{202}$), consistent with our chosen upper limit. Most of the compounds in the compilation have ΔH_{vap} values significantly lower than this.

R1.3. Results presented here are important in understanding the difficulties in reproducing appropriate volatility distributions. The text however is rather difficult to follow in places and I personally had to keep double checking results in places. I appreciate the discussion of quite detailed results is hard, but it may help the reader to present a series of bullet points summarizing the constraints which enabled reconciliation between model/measurements before a general discussion.

We have edited the manuscript significantly to make it overall more readable.

R1.4. On page 1914 the authors make the statement that: 'For example, the addition of a single ketone function group to a straight-chain hydrocarbon decreases the vapor pressure by approximately a factor of 10, the addition of an alcohol group by a factor of 100 and the addition of a car-boxylic acid group by a factor of 1000 (c.f. Fig. 1b in Goldstein and Galbally, 2007).' This statement is a bit sweeping. The context in which the authors are using this rule of thumb would suggest that as it doesn't refer to multifunctional compounds. Providing it is clear that the factors of 10, 100 and 1000 are very approximate then the statement is OK. However, whilst it may be true for straight chain hydrocarbons, it is risky to extrapolate this behavior to multifunctionals. Chattopadhyay and Zieman (2005) see extra alpha hydroxy groups raising the vapour pressure. Results from Knudsen effusion also show perhaps unexpected behaviour with extra OH groups and single ketone groups with regards to the subcooled vapour pressure, which is raised rather than lowered by extra groups. This is probably due to intramolecular bonding.

The manuscript has been edited to make is clear that this indeed a very approximate generalization. We have added brief discussion to the studies mentioned by the reviewer to make

it clear that unexpected behavior can certainly occur when multifunctional compounds are considered.

R1.5. Conclusions. The overview of findings presented in this study is great. Using variations of the volatility basis set as a relatively detailed diagnostic tool is interesting and should be included in future studies. It would be good if the authors could comment on the general applicability of this approach in future field campaigns and what limitations there may be dependent on the environment studied...if this is possible to predict?

We believe that this approach should be broadly applicable to any future measurements. We do not foresee any particular limitations of the method, assuming that the data quality is sufficiently high. For example, it is generally useful to use average thermograms as this helps to mitigate the effects of any changes in the prevailing conditions that might occur during the collection of a single mass thermogram. Also, in regions where the OA fraction of the total aerosol is small it may be necessary in future analyses to explicitly account for the presence of “other” components (e.g. sulfate, BC, nitrate, etc.), although such an extension would benefit from complementary measurements as to the mixing state of the sampled aerosol.

Response to Reviewer #2

R2.1. Page 1907: What is the averaging process used to obtain average thermograms? Is it possible that a simple arithmetic average is not appropriate for these nonlinear profiles and leads to some kind of artifacts? It would be interesting to compare analyses of two thermograms and then their average.

The presented measured mass thermograms are simple arithmetic averages from the entire campaign. It is not clear how this averaging procedure would lead to any specific artifacts, but we do note here that a certain amount of information content is lost by only considering the campaign averages. It could be interesting for future studies to investigate how e.g. the HOA or OOA mass thermograms differ with time of day, day of week, ambient loading, etc.

R2.2. Page 1910: Is the result with $C^* = 10^{-15}$ $\mu\text{g}/\text{m}^3$ different from 10^{-14} or 0? I ask because this C^* value corresponds to ~ 1 molecule/ m^3 of air, which means that for the flow rate of 0.6 LPM and 160 min measurement period, in which 0.1 m^3 of air is sampled, ~ 0.1 molecules would pass through the thermodenuder. How can the result be sensitive to this value?

It is important to keep in mind that the C^ values given here are for ambient temperature (25°C). The C^* values all increase with temperature. For example, for the compound with $C^* = 10^{-15}$ $\mu\text{g}/\text{m}^3$ the $\Delta H_{\text{vap}} = 200$ kJ/mol (due to the imposed upper limit). Thus at 200°C the C^* has increased to $\sim 10^{-2}$ $\mu\text{g}/\text{m}^3$. Because all of the very low volatility compounds will have the same ΔH_{vap} value (again, due to the imposed upper limit), the proportional increase will be the same, i.e. a compound with $C^*(25^\circ\text{C}) = 10^{-14}$ $\mu\text{g}/\text{m}^3$ will increase to $\sim 10^{-1}$ $\mu\text{g}/\text{m}^3$ at 200°C, etc. This is the reason that the results are sensitive to the exact choice of $C^*(25^\circ\text{C})$.*

R2.3. Page 1912: Does a meaningful comparison of the volatility distributions reported here with those in the literature for different systems require that the data be analyzed using the same methods and assumptions (such as evaporation coefficient)?

Whether other systems requires similar assumption depends on the method used to derive volatility distributions. For nominally equilibrium studies (such as smog chamber studies), the kinetics of evaporation will not be of significance and thus the evaporation coefficient is not important to consider. However, if temperature dependent experiments are used to infer volatility distributions (whether equilibrium experiments or otherwise) consistent choice of ΔH_{vap} is very important to allow comparison between different studies. For studies that rely on evaporation kinetics (such as other TD studies) to derive volatility distributions, the use of a similar evaporation coefficient, diffusivity, etc. is indeed important if results are to be compared.

R2.4. Page 1914: I am more concerned than the authors about the possibility that heating impacts oligomer formation. This will depend on the particular reaction. One would expect that ester formation from reactions of organic acids and alcohols would be enhanced with heating since the reaction involves loss of water. On the other hand, hemiacetals may decompose at higher

temperatures since the reaction is a simple, reversible dissociation to an alcohol and aldehyde and would be enhanced by the favorable entropy increase.

It is certainly possible that heating can affect the particle chemical composition from processes other than evaporation (as discussed by the reviewer). The model as implemented is not capable of quantitatively (or even qualitatively) assessing the effects of such particle-phase chemistry as we have relied on model/measurement comparisons to derive our volatility distributions. Although an important consideration, greater understanding of the influence of chemistry in TD's awaits further experimental efforts. In our brief discussion of the potential influence of in TD chemistry we now mention that some reactions might lead to an increase in volatility (decomposition) while others could lead to a decrease in volatility (accretion reactions).

Technical Corrections

R2.T1. Page 1915, line 3: "this" should be "these".

This has been done.

Response to Reviewer #3

R3.1. The effective saturation concentration (C^*) spectrum (as it is currently used in the model) for a given POA, SOA, or ambient data is strictly valid only under the conditions (i.e., aerosol composition, RH, and T) the spectrum was obtained. For example, an oxygenated organic compound may have a high C^* value over diesel POA, but its C^* value may be much smaller over a highly oxygenated SOA or over aqueous ammonium sulfate solution. Similarly, a hydrophobic/non-polar POA (such as lubricating oil aerosol) may not absorb oxygenated SOA species, thereby considerably increasing the C^* values of such oxygenated organic species over hydrophobic POA and vice versa. Glyoxal is a good example of a compound whose C^* depends strongly on the aerosol composition and possibly also the ambient relative humidity. Volkamer et al. (2007) showed that the glyoxal imbalance between the expected and observed levels in Mexico City corresponds to several $\mu\text{g m}^{-3}$ of equivalent SOA mass, and can explain at least 15%

of the SOA formation. The model as it stands, does not appear to take into account such aerosol composition and relative humidity effects on the C* spectrum. Can the authors comment on the potential effect of this assumption on their results?

The basis set formulation is not compound specific, but instead effectively “lumps” compounds with similar volatilities into the same bin. In this manner, factors such as aerosol composition and relative humidity effects are inherently accounted for, although we are not able to account for any changes to activity coefficients that may occur as the aerosol evaporates and the higher volatility compounds are distilled from the particle phase. If we were using a model in which individual compounds were considered then we could estimate the activity coefficients for each component from theory (e.g. Bowman and Melton, 2004). However, within the basis set formulation such theoretical estimates are not appropriate. Also, it must be kept in mind that the analysis presented here deals only with the campaign average mass thermogram. Thus, differences resulting from composition/relative humidity differences are averaged out. It is certainly possible that the volatility (and therefore the observed mass thermogram) will differ for similar components (e.g. HOA, OOA) in different regions and at different times as a result of the prevailing conditions. The model introduced here can, in theory, be used to explore these observed differences. For example, mass thermograms obtained from different regions can be individually analyzed and, if significant differences are observed, this may be attributable to differences in the activity coefficients or the compounds comprising the aerosol in the different regions. Alternatively, if higher time resolution mass thermograms are considered (i.e. daily or weekly averages as compared to the campaign average), observed differences can again be attributed to differences in activity coefficients or actual chemical composition. If, for example, the effective vapor pressure of glyoxal changes as a function of the prevailing conditions this will be observed as a change in the measured mass thermogram. The model would interpret this as a shift in the aerosol mass between vapor pressure bins, but cannot by itself be used to determine the reason for this change. What the model can do is assist in the quantitative interpretation of observed differences in measured mass thermograms. In a sense, it seems as if the point the reviewer is getting at is how representative is the campaign average mass thermogram and what information does using such a long average effectively mask, which is beyond the scope of the

present work. Future studies where the temporal variability in measured mass thermograms is considered would certainly be of interest and could help to shed light on the reviewers question.

R3.2. Page 1905, line 6: $C_{i,sat}$ has not been defined. Should it be C_{i}^* instead?

Yes. This has been updated.

R3.3. What is the relative humidity at each measurement point shown in Figure 1?

The presented observed mass thermogram is the campaign average, and therefore the relative humidity at each point will be approximately the same since the sampling time for a single mass thermogram is ~3 hrs.

R4.4. At what temperature is each volatility distribution in Figure 2?

The distributions are given for 25°C. This will be stated.