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Atmospheric
Chemistry
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Discussions

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.

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1. *The authors explain the analysis method used for combining TD-SMPS and TD-AMS data sets from FAME-2008 to construct a volatility distribution of organic aerosol. The introduction including the review of denuder history is quite nice, succinct, and informative. The overall manuscript is easy to follow and well written. The overall balance between science and technical is heavy on technical and light on atmospheric science. AMTD rather than ACPD could be the more appropriate venue for publication. In this regard, the title and content of the manuscript seem not to match.*

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Our paper combines the continued development of a technique for the analysis of thermodenuder field measurements and its application to highly aged organic aerosol. It is part of a series of papers for the FAME-08 study (Pikridas et al., 2010; Hildebrandt et al., 2010; Engelhart et al., 2010) already published in ACP or ACPD in the EUCAARI special issue. While the paper is probably suitable for both ACP and AMT, our preference would be to keep it in ACP in the same special issue as the rest of the FAME-08 papers.

2. *There is a major omission in this manuscript in that the fundamental assumption of the absence of reaction inside the particle is not stated. Several thermodenuder studies have emphasized the occurrence of particle phase reactions at the elevated temperatures in thermodenuders, both for ambient as well as laboratory aerosols. Examples include:*

Denkenberger, K. A., R. C. Moffet, J. C. Holecek, T. P. Rebotier, and K. A. Prather (2007), Real-time, single-particle measurements of oligomers in aged ambient aerosol particles, Environ. Sci. Technol., 41, 5439-5446.

Wu, Z. J., L. Poulain, B. Wehner, A. Wiedensohler, and H. Herrmann (2009), Characterization of the volatile fraction of laboratory-generated aerosol particles by thermodenuder-aerosol mass spectrometer coupling experiments, J. Aerosol Sci., 40, 603-612.

This omission is critical. For example, Figure 8 that goes with the title of the manuscript is especially problematic. The figures before Figure 8 show MFR vs. temperature, so these are observations, even if underlying effects are not fully known. But Figure 8 places a framework around these observations by using an enthalpy to estimate room temperature volatility from observations at elevated temperatures. This is the process of translating the observations into the representative bins for panels B and D. This representation is potentially very wrong if there are considerable particle phase reactions at elevated temperatures, as the recent literature suggests. The authors

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make no mention of this complicating and perhaps even dominant phenomenon that would potentially completely invalidate Figure 8.

We agree that this is an important assumption for all thermodenuder measurements and it has been used by all recent thermodenuder studies (see for example Huffman et al., 2009; Jonsson et al., 2007; Kostenidou et al., 2009). In our work we have tried to avoid the very high temperatures (above 200 C) that are traditionally used in thermodenuder measurements by using instead higher residence times. However, the point of the reviewer is well taken: even at 110 C, where a lot of our measurements were made, there is a significant probability of reactions inside the particles. This point is stressed in the revised paper and the corresponding citations have been added. It is now included in both the abstract and the conclusions of the paper given that our interpretation of the measurements is based on this assumption.

3. *Equation 1 for calculation of density is not correct because densities add as inverse quantities for mass fraction. This could just be a typo, i.e., the stated equation would be correct for volume fraction. But if the written equation was the one used in the analysis then this could be a point of error.*

There is a typo in the equation that has been corrected in the revised paper. The correct equation (include in the original paper by Kostenidou et al., 2008) has been used in the analysis.

4. *A seemingly important citation to Epstein et al. mentioned in several figures is not found.*

The missing reference has been added.

5. *The claim in the abstract of ambient aerosol being two orders of magnitude less volatile than laboratory SOA is an overstretch because in point of fact the manuscript compares only to one laboratory system, which is the dark ozonolysis of alpha-pinene.*

Our measurements of the volatility of monoterpene (a-pinene, b-pinene, and limonene) SOA produced under a variety of conditions (low and high NOx, low and high RH, etc.) support this claim (Lee et al., Volatility of secondary organic aerosol from the ozonolysis of monoterpenes, Atmos. Environ., in press). This is now explained in the paper to avoid misunderstandings.

6. *Page 17438, line 18, phrasing and citations could be revised because present version suggests that the citations on line 19 are related to the use of thermodunders. In fact, they relate only to the AMS.*

We have rephrased this sentence.

7. *Page 17442, line 21, this sentence does not make too much sense, i.e., slope needs to be stated to support the argument. Right now, the statement is that* R^2 *= 0.95 without a statement of slope so "agreed well" cannot be concluded from provided information.*

The fact that the slope was 1.09 has been added to the text.

8. *In Fig 7 and Fig 9, there are only 3 data points for 105 sec but 10's of data points for 14 sec. What implication does this difference in the quantity and quality of empirical information have for conclusions? Similarly, the temperature range is 100 to 140 C but the model is applied with extrapolation from 30 to 100 C. The analyzed data sets seem sparse and not well balanced.*

This is a good point. The measurements were designed to explore the link between OA composition (as measured by the AMS) and its volatility. So we decided to concentrate in measurements at around 110 C corresponding to the evaporation of roughly 50 percent of OA. 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 Figures 7 and 9 represents an average of approximately 20 hours of measurements we think that our results are robust. Please note that during the fitting the measurements at the different residence times were given the same statistical weight in the fits. Also the measurements were averaged over each 2 C. These steps have improved the balance of the dataset used for the modelling part of the work. This discussion has been added to the revised paper.

9. *Would the authors confirm that the data points for 14 sec and 105 sec in Figs 7 and 9 were collected nearly simultaneously from the same air mass? That is, if the data were collected on different days and the mass spectra are different, then the comparison is problematic.*

The data points for the two residence times were collected in the same air masses. However, the advantage of the study (as mentioned in our response to the previous comment) was the little variability in the OA spectrum during the full study (Hildebrandt et al., 2010). There was little variability in the AMS spectra with the air mass origin. There was also little variability of the measured volatility (Figure 7). This clarification has been added to the revised paper.

10. *The summary comment is that the content and tone of manuscript are more appropriate to AMTD rather than ACPD. If transferred to AMTD, some of the questions above indicate significant re-working of the manuscript is necessary. The aspects related to the sparseness of the data set might not be able to be overcome as a standalone manuscript. A workaround could be that the content of this manuscript should not appear separately but instead as a section within a more comprehensive manuscript that includes other aspects related to FAME-2008.*

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We think that the sparseness of the data set is not a significant problem given the practically constant OA AMS spectrum during the study. The data set is actually quite big (a full month of AMS and thermodenuder measurements). The AMTD versus ACPD choice has been addressed in our reply to the first comment of the reviewer.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 17435, 2010.