Atmospheric
Chemistry
and Physics
Discussions

Open Access

EGU

Interactive comment on "Organic aerosol in the summertime Southeastern United States: Components and their link to volatility distribution, oxidation state and hygroscopicity" *by* Evangelia Kostenidou et al.

Evangelia Kostenidou et al.

spyros@chemeng.upatras.gr

Received and published: 18 March 2018

(1) *The manuscript 'Organic aerosol in the summertime SE US: Components and their link to volatility distribution, oxidation and hygroscopicity' by Kostenidou reports on ambient aerosol measurements using a HR-TOF-AMS coupled to a thermodenuder inlet. Total submicron non-refractory OA was split into four main factors: BBOA, Isoprene-OA, MO-OOA and LO-OOA. The observed thermogram profiles of OA and of each of its four factors are shown, along with the modeled volatility distribution of the components of the sum and the four factors. Lastly, an attempt to reconcile hygroscopicity,*

O:C and volatility is made. The results presented will make an important contribution to the existing body of knowledge on the composition of OA, specifically, the OA present in a moderately-polluted biogenic-rich region of the SEUS. One potential issue needs to be addressed, and a few other clarifications need to be made for this work to be published.

Our responses to the comments of the referee and the corresponding changes to the paper can be found below.

(2) *An interesting observation using this TD-AMS setup from SOAS was that the MO-OOA exhibited a lower MFR subsequent to heating compared to the LO-OOA component of OA. That is, more of the 'more oxygenated' component had evaporated or been destroyed by heating relative to the 'less oxygenated' component. A more detailed explanation for this phenomenon than what is currently provided (essentially referencing the work of Karnezi et al.) is needed. How does the model predict that MO-OOA was composed of less volatile material compared to those of LO-OOA? What observation or information was fed into the Karnezi model, etc.? For instance, MO-OOA and Isoprene-OA appear to exhibit distinct MFR thermogram profiles (figure 2), which the Karnezi model is able to reproduce well. Yet, MO-OOA and Isoprene-OA possess nearly indistinguishable C* versus mass fraction distributions (figure 3). How is the model able to come up with essentially the same composition for two OA factors that exhibit distinct thermogram profiles? One conclusion the authors draw from this MO vs LO thermogram observation is that MFR alone can be misleading. So I assume the authors relied on the model to be the arbiter. What exactly was the contribution of TD?*

This is an excellent point. It has often been assumed that a lower MFR means more volatile OA and vice versa. This is correct, but it applies to the temperature of the measurement. The volatility of an OA component at a given temperature in the TD depends not only on its volatility at ambient conditions (the ones that we are interested in), but also at its enthalpy of vaporization. A high enthalpy of vaporization leads to

drastic increases of the volatility as the temperature increases. The enthalpy of vapor-
ization does affect significantly the slope of the thermogram over the full temperature
range. The Karnezi et al. algorithm looks at all potential explanations for the observed
behavior and it reports them. These results are shown in Figure 3. The model finds
that the observed behavior of the thermograms is probably due to differences in the
effective enthalpy of vaporization (higher value for the MO-OOA than for the LO-OOA).
This difference appears to be robust considering the estimated uncertainties (Fig. 3e).
The model uses the observed MFR, the concentration of each factor, and the size of
the particles as inputs for its analysis. We have added the above discussion in the
paper.

The estimated effective enthalpy of vaporization also explains the similarity of the es-
timated volatility distributions of MO-OOA and Isoprene-OA. However, in this case
please note the significant uncertainties of especially the Isoprene-OA volatility dis-
tribution for all bins. There are solutions for which for example the MO-OOA is a lot
less volatile than the Isoprene-OA. So the measurements in this case are not sufficient
to compare the volatility of the two factors. This is the reason that we did our best in
the paper to avoid strong conclusions about comparisons of the volatility of the various
factors. This is now stressed in the Conclusions of the paper.

Indeed the model was the arbiter for the analysis. However, the model was constrained
by the TD measurements as well as the other measured inputs (OA and factor concen-
trations determined by the AMS, size distributions, etc.).

(3) *Are you able to calculate a C* versus mass fraction distribution at each thermogram
temperature setting? Determining how the C* of the material that compose a given OA
factor evolves as it is incrementally heated would provide an important constraint.*

This is a good suggestion. We added the predicted composition in terms of C* of
each factor after passing through the thermodenuder as a function of temperature.
We have added a new graph to Figure 1 for the composition of the total OA and we

have also added a new figure (Figure 4 in the revised paper) for the composition of the four factors. The model predicts, as expected, that the less volatile material with $C^*=0.1$ μg m^{-3} dominates the composition of the remaining aerosol after the TD as the temperature increases for all factors. However, there are significant differences in the evolution of the composition of the various factors. A short discussion has been added together with the new figures.

(4) *Comparison to previous work on OA measured during SOAS needs to be more focused. A thorough comparison (and explanation of why there seems to be a discrepancy) to the work of Hu et al. is more appropriate here as the two utilized the same approach (TD-AMS). For instance, how do the factor assignment (BBOA, Isoprene-OA, MO-OOA, LO-OOA) compare to that of the Jimenez group? That data is publicly available and comparison to it should be included in the analysis. In comparing against the works of Saha and Lopez-Hilfiker, a discussion of how different techniques can yield different observations or interpretations is more suitable. For instance, the thermogram profiles obtained from shown by Lopez-Hilfiker et al. show residual IEPOX signal desorbing off the FIGAREO-CIMS inlet well above 100 C whereas the TD-AMS saw none above 100 C. Suggesting artifact in another method without supporting evidence is not justified.*

Hu et al. (2016) also used a thermodenuder in order to estimate the Isoprene-OA and the total OA volatility distribution. Even though they used practically the same measurement technique as we did, their approach for the measurement interpretation was very different. Hu et al. (2016) used the empirical method of Faulhaber et al. (2009) and not an aerosol dynamics model for the estimation of the volatility distributions from their MFR measurements. Their method is based on a relationship between TD temperature and organic species saturation concentration at 298 K (C^*) that has been obtained using 5 compounds (acids) with known saturation concentration. This approach is applicable to organic compounds with similar properties (e.g., enthalpy of vaporization) to the 5 known compounds, but it may encounter significant difficulties

for OA that is quite different from the model compounds. A related weakness of that approach is that it does not account for the enthalpy of vaporization as the model used in this work does. We have added this discussion in the text.

Hu et al. (2016) (if this is the paper that the reviewer is referring as Jimenez et al. group) presented results only for the IEPOX-OA and total OA. These results are compared to ours in Figure S6.

Please note that the Lopez-Hilfiker et al. (2016) results, as explained in the text (lines 418-430 of the original manuscript), are strictly for the IEPOX SOA which is a subset of the Isoprene-OA investigated here. So a quantitative comparison of the corresponding volatilies is not possible. Also, the analysis of Lopez-Hilfiker et al. (2016) does not account for the effect of the vaporization enthalpy. There is also a potentially important experimental difference in this case, as in our work the OA just evaporates in the TD, while the Lopez-Hilfiker et al. (2016) experimental approach involves collection of the OA on a filter and then heating and desorption. We have added additional discussion of these differences to the revised paper.

Saha et al. (2017) obtained the total OA thermogram using a thermodenuder system and then estimated the corresponding volatility distribution using an aerosol dynamics model and the volatility basis set (Donahue et al., 2006; Lee et al., 2011; Saha et al., 2015; Saha and Grieshop, 2016). Their experimental and data analysis approach is a lot closer to ours compared to Hu et al. (2016) and Lopez-Hilfiker et al. (2016) and their results for the total OA are quite consistent with ours. Their model takes into account the vaporization enthalpy as well and this is probably the key difference among the various approaches. This issue is now discussed in more detail in the paper.

(5) *Why do the abundance distributions predicted for the OA factors (Figure 3a-3d) look the way the do? That is, why do those for MO-OOA, LO-OOA and isoprene-OA appear to be bi-modal, whereas that of BBOA is not? Perhaps it is this arbitrary designation into three log base-10 bins that obscures the real distribution? Can the distributions be*

shown on finer C* scales? What is the lower limit of C* that can be detected with this approach? But basically, what is the source of the low volatility material as opposed to the high volatility material? OH versus O_3 versus NO_3? Aging? Is there an atmospheric chemistry explanation for the calculated volatility distribution?

The selection of the three volatility bins was not arbitrary, but was based on the ambient measured concentration and the available TD data (the number of selected temperatures). This issue is also discussed in our response to Comment 2 of Referee 1. One can use additional bins in the fitting algorithm either extending the range or providing additional resolution, but the results will be meaningless (e.g., fitting four measurements with a model using five or more parameters). With only three volatility bins and the corresponding uncertainties a more detailed analysis of the shape of the distributions will not add much to the paper.

In theory, the TD approach can go down to concentrations as low as 10-5 μg m^{-3} or even lower if a high enough temperature is used. For example, Louvaris et al. (2017) used temperatures up to 400 C. Of course, the major problem is that use of higher temperatures may lead to a series of reactions in the aerosol phase (fragmentation, etc.) introducing considerable uncertainty in the corresponding measurements. The temperature and corresponding volatility range used in this study are considered relatively "safe" even if artifacts due to reactions are still expected even in this relatively low temperature range. We have added a few sentences explaining this point.

The AMS cannot provide detailed information about the identity of the compounds in each volatility bin. Use of other chemical analysis techniques is required and would be extremely helpful in linking the volatility distribution with atmospheric processes. This is now mentioned in the Conclusions section.

(6) *The error bars shown in Figures 1 and 2 indicate there is little variability in the thermogram profiles throughout the SOAS campaign. Have the authors looked for any dependence of the steepness of the thermogram profiles on time of day, high/low OA*

loading, RH, temperature, particle acidity, high/low NOx, etc, all of which varied widely through the duration of SOAS?

We have followed the suggestion of the reviewer and examined the correlation between the MFR of each factor at each temperature with the RH, temperature, O_3, NO, NO_2, acidity and OA loading. In addition, we checked the diurnal profiles of each factor at each temperature.

There was a tendency of the MFR of all factors at higher temperatures to increase as the ozone concentration increased. For example, the R^2 between O_3 and the MFR of MO-OOA at 80 C was 0.25, R^2=0.36 for the MFR of LO-OOA at 100 C, R^2=0.26 for the MFR of Isoprene OA at 100 C and R^2=0.22 for the MFR of BBOA at 100 C. This suggests that when the photochemistry is more intense the OA evaporates less in the TD. The R^2 between the acidity and the MFR of LO-OOA at 100 C was 0.26, suggesting that acidity may be also affecting the MFR. The MFR of BBOA at 100 C on the other hand was anti-correlated to the NO and NO_2 concentrations (R^2 of 0.23 and 0.37 correspondingly). This indicates that at lower NOx levels (away from the source) BBOA evaporated less, suggesting that this factor may contain both fresh and aged BBOA or fresh BBOA aerosols mixed with aged background. This is also supported by the relatively high O:C ratio of this factor (0.58). All the other R^2 values examined were lower than 0.2.

There was no distinct diurnal profile for the MO-OOA, BBOA and Isoprene-OA MFR. For LO-OOA MFR at 80 C and 100 C there was a slight increase (with a lot of noise though) between 11:00-16:00. As a result, we do not have much evidence to support a significant diurnal variation of the MFR of the various factors.

We have added a paragraph in the manuscript describing the above results.

(7) *A strong point was made that the findings of Jimenez et al. (2009) had been contradicted, but no thorough explanation for the possible reason for the discrepancy.*

Our conclusion is that the proposed relationship of Jimenez et al. (2009) does not apply to all environments and especially when multiple aerosol sources and types are present. One possible reason may be that the O:C-hygroscopicity relationship may not be monotonic, but there may be systems for which the relationship may be highly nonlinear. For example, Cain and Pandis (2017) showed that the hygroscopicity could exhibit a maximum at intermediate volatilities. This suggests that the relationship between the hygroscopicity and the volatility may also be highly nonlinear. We have added a few sentences in the Conclusions discussing this point.

(8) *References made in some of the SI figures are not in the SI citation list.*

We have added the citations to the work of Karnezi et al. (2014), Nakao et al. (2017), Ulbrich et al. (2009) and Xu et al. (2015).

Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2017-1010, 2017.