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Atmospheric
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Interactive comment on "Volatility of organic aerosol and its components in the Megacity of Paris" *by* A. Paciga et al.

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(1) *The manuscript describes measurements of aerosol volatility during summer and winter campaigns at an urban background site in Paris. The authors derive volatility basis sets (VBS) for the total organic aerosol mass and for different identified organic aerosol fractions (or rather, PMF factors), such as HOA, OOA, etc. The presented material is interesting, but there are several points regarding data analysis procedure that need to be addressed prior to publication. My main concern is with the use of the mass fraction remaining (MFR) to judge aerosol volatility, which could have affected the data analysis. I understand that the MFR is currently the most popular representation of aerosol volatility. However, it is practically meaningless in terms of both thermodynamic or kinetics aspects of aerosol evaporation. It is trivial to show that aerosols*

that have the same thermodynamic properties, but different initial concentrations will demonstrate completely different MFR-based "volatilities" at the same experimental conditions (i.e., residence time in a TD). Thus, using MFRs to judge differences or similarities between groups of observations, for example between low and high concentration observations (e.g., p.22268 l.25 and Fig.S1), could be prone to errors. The authors have a model to derive the actual volatility properties (VBS). The derived VBSs should be used instead of relying on a vague comparison of MFRs ("differences are within experimental variability", p.22268 l.26). The VBS of the two groups may very well be similar, but one needs to do a comparison of the VBS to make such a claim. I suggest the authors revisit their data selection criteria using the VBS representation of aerosol volatility instead of relying on MFR.

We do agree with the point of the reviewer and this is exactly what we tried to accomplish in our paper. The mass fraction remaining is the measured quantity, but as the reviewer mentions it depends not only on the volatility distribution of the aerosol, but, for a given TD, also on the particle size distribution, enthalpy of evaporation, any mass transfer resistances to evaporation, etc. Our limited discussion of the MFRs was intended only as a zeroth order analysis of our measurements. All our conclusions are based on the evaporation model that has been used for the interpretation of the MFR measurements. We have made changes to the original manuscript to make sure that it does not leave the impression that we rely on the MFR data alone to draw conclusions about the volatility distribution of the aerosol. We do clarify in the introduction of the paper that the MFR depends on several aerosol properties and of course the TD residence time.

Other comments

(2) *p.2267, l 21: was the flow through the TD adjusted as a function of temperature or does 25 s residence time refer to the flow at room temperature? Is there any reason why the centerline residence time is given instead of the mean residence time? I un-*

derstand that the centerline residence time can be used to derive the mean residence time for an ideal laminar flow. The actual flows are, however, often non-ideal. I assume that the mean residence time was used in the model, thus it would be more appropriate to report its values instead of that for the centerline.

The flow rate remained constant during the operation of the thermodenuder and the reported value corresponds to 298 K. We also report now both the centerline and the mean residence time in the TD. We have clarified these important points in the revised manuscript.

(3) *p. 22268, l.20. The sentence "The correction efficiency. . ." does not follow from the previous sentences and should be moved up. Was the collection efficiency the same for both campaigns?*

The reported collection efficiency of 0.5 corresponds to the winter campaign (Crippa et al., 2013a). An average value of 0.38 was estimated for the summer campaign (Crippa et al., 2013b). We have moved this sentence about the collection efficiency during winter to a new paragraph earlier in the section where we discuss the AMS data analysis for both seasons.

(4) *Figure S1 and the accompanying discussion. As discussed above, I do not agree with the argument that if MFRs are similar for two groups of observations then the two groups have similar volatility properties. Given that the two groups were selected based on the aerosol concentration, I would actually expect that similarity in their MFRs indicates differences in their volatility (VBS).*

We think that the objection of the referee is due to a rather confusing sentence. We have rephrased this to: "To evaluate whether the OA during these higher concentration periods has different MFR than during the rest of the campaign, we separated the data in two groups using an OA concentration cut-off of 1.5 μg m^{-3}". Please also note that the differences in the absolute concentrations are rather small (a few μg m^{-3}) and

therefore the effect of the organic aerosol concentration on the measured MFR is very small in this concentration range.

(5) *p. 22269, l.5. I am not sure why the data needed to be averaged to 5-degree temperature bins. This brings a question how exactly was the TD operated (was the temperature scanned?). This information should be added to section 2.1.*

The TD scanned the temperature range from approximately 20 to 200 C using different intermediate sampling points. The small temperature differences in the day to day operation during these two month-long campaigns generated data at temperatures differing by a few degrees and necessitated the averaging to 5-degree temperature bins. This is now explained in Section 2.1.

(6) *p. 22269, l.18-20. I do not understand this sentence, especially the part ". . .for which several MFR measurements exceeded significantly unity". The MFR by definition cannot exceed 1.*

During low factor concentration periods both the numerator and the denominator of the MFR are extremely uncertain (one is dividing something close to zero with something else close to zero) and therefore values of MFR exceeding unity are sometimes calculated. These are of course meaningless and are a clear sign that the factor concentrations are too low to be used in volatility measurements. We have taken advantage of this behavior to define the factor concentration thresholds (see Table 1) below which the error of both the TD measurements but the corresponding PMF analysis do not allow reliable measurement of the MFR. This important point is now better explained in the end of Section 2.2.

(7) *p. 22271, first paragraph. I suggest the authors compare VBS for the total OA, not the MFRs. Given the degree of variability, the statement that "differences are mostly* *noticeable at the high temperatures" needs to be backed by an estimate of statistical significance of the observed differences.*

This is a good point. We have added a new figure comparing the OA volatility distributions for the summer and winter. The results suggest that the two volatility distributions are quite similar to each other. Considering the uncertainty of the corresponding volatility distributions the differences at high temperatures (e.g., corresponding to the less volatile components) are not statistically significant. The corresponding sentence has been deleted.

(8) *p. 22271, l.9 and other instances in the text. Just as the MFR, T50 depends on the aerosol concentration. The authors use this parameter to compare, for example, volatility of different PMF factors, even though concentrations of these factors are quite different (p.22271.25-26). Such comparisons are quite meaningless.*

This is a valid point and we have deleted the corresponding sentence about the potential similarity of the volatility distributions. This similarity is shown later using the actual estimated volatility distributions (see also our response to Comment 7 above). We would like to keep the presented T50 values as they do provide a zeroth order summary of the thermogram.

(9) *p.22272, l. 11. More information needs to be provided on how VBSs were derived for individual factors. It is stated that thermograms for individual factors (Fig.S3) were fitted using the model. This suggests that the factors were assumed to be externally mixed. If this is so, how justified is this assumption, are all factors assumed to have the same size distribution? If the factors were assumed to be internally mixed, then some justification for this procedure, i.e., fitting individual thermograms, needs to be provided. I would assume that co-evaporation of other factors would affect the thermograms and thus the derived VBSs.*

The reviewer makes an interesting point. Given that the AMS factor analysis is based

on bulk measurements, we had to assume that all OA components (factors) had the same size distribution. The individual fitting of the thermograms of each factor is equivalent to assuming an external mixture of the various factors and implicitly neglecting the co-evaporation of these factors. These two assumptions are now clearly stated in the revised manuscript. We have added a paragraph discussing the sensitivity of our results to these two assumptions.

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