

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

Anonymous Referee #2

Received and published: 16 November 2015

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

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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.

Other comments.

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 understand 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.

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?

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).

p. 22269, l.5. I am not sure why the data needed to be averaged to 5-degree temper-

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ature bins. This brings a question how exactly was the TD operated (was the temperature scanned?). This information should be added to section 2.1. 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.

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.

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.

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.

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 22263, 2015.