Response to Anonymous Referee #1

(1) The authors report results from measurements of organic aerosol volatility, as characterized through measurement of the loss of OA mass due to evaporation as a function of temperature, for ambient particles sampled during winter and summer in Paris, France. They present results both for the total OA behavior, as well as for the behavior of specific OA "factors" determined from positive matrix factorization. They ultimately find that the average OA volatility is not all that different between winter and summer in Paris, but that there are distinct differences in the OA factor volatilities within a given season and between the same factors in different seasons. These differences are discussed briefly in terms of differences in chemical composition, as reflected from likely source attributes and obtained mass spectra of the OA factors. Overall, this study contributes new information regarding the volatility of ambient OA, but it could do a better job of putting their specific results in the context of literature results. Additionally, I believe that the data associated with the OA factor volatilities could be presented in a more tangible way to the reader, and suggestions are provided as to how to do this. I have some concerns regarding the averaging procedures used in terms of how they may/may not introduce any particular biases into the analysis. I suggest that this work is ultimately publishable, but should be considered further after revision.

We appreciate the constructive assessment of our paper by the referee. These individual comments are addressed below.

Specific comments:

(2) The authors report measurements of the mass fraction remaining, which was determined from measurements made alternately every 5 minutes sampling through the TD or ambient particles. However, it is not made clear exactly how the ratios were calculated. Were they calculated using just measurement pairs (e.g. the measurement at t-1 divided by the measurement at t) or were they calculated using an average of TD measurements made before and after each ambient measurement? Or an average of ambient measurements made before and after each TD measurement? To some extent, all of these details may cancel out after sufficient averaging, but the normalization process can certainly impact the apparent amount of atmospheric variability, as shown in Fig. S1. The normalization procedure is less of a concern when atmospheric conditions are constant, but when things are changing rapidly (and here, rapidly means on 5-15 minute time scales) the method used can matter a lot. Can some of the "atmospheric variability" in Fig. S1 be explained away as a result of the normalization procedure used? Have the authors considered, for example, filtering their measurements based on the extent of change between two sequential ambient points? I believe that such considerations are particularly important in the splitting of the dataset into high/low concentration periods since visual examination of Fig. 1 suggests that there is generally greater atmospheric variability (faster changes) during the high concentration periods than during the low concentration periods. Ultimately, I believe that the authors need to at minimum be more specific as to how their MFR values were calculated.

The MFR values were first calculated using measurement pairs (the measurement at interval *i* divided by the measurement at interval *i*+1) and then they were further averaged resulting in Figure 3. The final averages were relatively insensitive, as the reviewer guessed, to the details of the individual MFR calculation. However, the variability of the atmospheric conditions, once more as the reviewer suggests does introduce variability in the individual MFR estimates. We had the same concern as the referee regarding the variability of the MFR during the high concentration periods and this was one of the motivations for splitting the dataset into high and low concentration periods. However our analysis did not find any differences for the corresponding MFRs during these two types of periods. We have added in the revised manuscript the information about the details of the calculations of the MFR and the variability that is introduced due to the variation of the atmospheric concentrations.

(3) P22267, L25: The authors mention the flows for the SMPS, stating at the end that the values selected ": : :extend[ed] the size-range of measured particle: : :". Extended relative to what? Had the SMPS been operated at 3 lpm sheath, 0.3 lpm sample, the range would have been "extended" even further? In other words, I don't find this statement necessary nor clear.
We have revised the corresponding sentence simply stating the operational parameters of the SMPS during these measurements to avoid unnecessary confusion.

(4) P22268, L26 and Fig. S1: The authors note the "experimental variability" and use this as a reason to not split the data set. I believe that this is reasonable, but at the same time it would seem to me that Fig. S1 could be presented as, for example, a box and whisker graph or as means and medians to help illustrate whether the average (or median) properties differed between the high/low periods. There is currently so much atmospheric variability that it is difficult (for me at least) to really conclude that there is no "discernable difference."
We do agree with the suggestion of the referee. In the revised paper we present the data in Figures S1 and S2 as box and whisker plots. The new Figure S1 does illustrate the similarity of the two data sub-sets a lot better.

(5) Section 2.2: The authors have ultimately averaged their data into 5 degC bins. It is not clear to me what guided this decision, as it is clear in looking at the rawer data (Fig.S1 and S2) that the data points are not equally distributed with respect to temperature. There are clearly a few temperatures that were favored, i.e. have lots of points, and many temperatures at which there are only a few data points. For example, it appears that the 100 degC bin might have 100's of points (or at least many 10s of points), whereas the 80 degC bin will only have a handful of points that make up the average. This means that the sampling is not equally weighted at all temperatures with respect to sampling period. For the winter data, such potential statistical issues visually look like they might not be particularly important, since they data show less overall variability compared to the summer data, where the variability can be quite large. Further, it appears that the TD operation was different between summer and winter, and thus the number of points sampled at especially the higher temperatures is quite different between the two studies, with (for example) many points at 150 degC for winter but very few in that same range for summer. I believe that the authors need to justify their 5degC bin choice and would actually recommend that they actually consider wider bins. Even 10 degC would be more justifiable that 5 degC, in my opinion. In any case, given that they have apparently binned their data into 5 degC bins, I am somewhat confused by the data presented in Fig. S3, for which the temperature points seem to be almost randomly distributed. But, perhaps this is simply an issue of there being some "missing" temperature ranges (where there was insufficient data?) that makes it seem like there is not a point every 5 degC. However, this still wouldn't explain why, specifically, the LVOOA thermogram has so many fewer points than any of the other thermograms given that the "percentage of measurements above threshold" for this factor is equal to or greater than those for HOA and COA, and very similar to that for MOA.

Our choice of the 5 C as the averaging interval was a compromise between averaging enough points at similar conditions and maintaining the dynamic behavior of the thermogram. While the choice of 10 C suggested by the reviewer is also reasonable, the corresponding analysis does not add anything new to the results or our conclusions. There were indeed different numbers of data points in each bin. This is taken into account into the calculation of the standard deviation of the mean for each temperature bin. During the first campaign we had a lot more measurements in specific intervals (e.g. from 80-100 C) in an effort to learn more from the corresponding variability. The corresponding efforts did not result in any significant insights and therefore during the second campaign we distributed the measurements more uniformly in the various temperature ranges. The missing points of the LV-OOA are from temperature bins with few measurements and very large corresponding uncertainties. We have added explanations of these points in the revised manuscript.

(6) It is indicated that PMF analysis was performed "combining both ambient and thermodenuded spectra" with a reference to Crippa et al. (2013) given. However, in reading Crippa et al., although it is noted that the AMS was operated with the TD, it is not clear whether the PMF analysis performed in that study was performed using the TD data as well. I suspect it was not. That would mean that the PMF analysis mentioned here is a new product, and as such the key aspects of the PMF analysis should be provided (perhaps as supplementary material), such as how the number of factors were selected, uncertainty estimation, etc.. Was the analysis performed here independent, or guided by the results of Crippa et al. already in terms of e.g. the number of factors obtained?

The analysis presented in Crippa et al. (2013) was performed using only the ambient measurements. This analysis was repeated for the purposes of this work combining the ambient and TD datasets. This second analysis was guided by the original results (e.g. the same number of factors was used) and produced for all practical purposes the same results for the ambient data for all factors. These are analyzed in great detail in Crippa et al. (2013) and adding the same information in the supplementary information here would not provide any additional insights. This information about the PMF analysis has been added in the paper.

(7) More information should be provided regarding the removal of MFR measurements. The authors state that "to minimize these problems, a minimum ambient mass concentration was determined for each PMF factor, based on the concentration range for which several MFR measurements exceeded significantly unity." How many is "several"? Are these continuous in time? Or spread throughout the entire campaign? Is this only considered when the TD temperature is greater than some value (such that the MFR would be expected to be much less than one, which may not be the case when temperature is close to ambient, e.g. <60C). And were any MFR values >1 observed above this criterion? If so, were they included or excluded from this analysis? It is not clear, but given the data shown in Fig. S1 and the extent of "atmospheric variability" for the "Peak Data" I suspect that all MFR >1 have been filtered from the data set. If so, this should be stated clearly. And I assume that the "several" criterion was consistently applied, but this should be stated and, if not consistently applied, justified. Further, it is not clear that the authors have considered the role of atmospheric variability in driving MFR values to be

>1 (which is dependent upon the normalization method applied). MFR values greater than unity can be an indication of working below the detection threshold, but they can also reflect the influence of atmospheric variability. The authors could possibly get at this issue by calculating an "effective" MFR value from just the ambient (or TD) measurements, where the "effective" MFR is the ratio between sequential ambient measurements, or the ratio between the average of two ambient measurements that are around a third and that central value. When this ratio deviates substantially from unity, either "atmospheric variability" or operating near the detection limit are having an outsized influence on the measurements. I say all this in part because it is unclear to me exactly why the threshold concentrations should be different in the winter versus the summer campaign. Did something change about the instrument?
We agree with the reviewer that additional discussion of the details of the removal of MFR measurements is needed. During low factor concentration periods the estimated MFR values could exceed 2 or they could be practically zero even at low TD temperatures. Also there was significant MFR variability from measurement to measurement. All of these are signs of problems due to the division of two very uncertain values. These problematic MFR values would be during certain periods lasting for a few or sometimes several hours and during all of them the corresponding factor concentration was very low. The factor concentration cut-offs corresponded to the appearance of MFR values exceeding 1.5 (usually a lot more than this). Small exceedances of 1 (say 1.1) were of course observed during measurements at low temperatures and were due to the uncertainty introduced by the estimation of the MFR from the ratio of two consecutive measurements. All the MFR values corresponding to concentrations lower than the thresholds of Table 1 were excluded from the analysis while all there rest (even if the exceeded one were used). Please note that the winter thresholds correspond to the left tails of the corresponding distributions (they correspond only to a few percent of the values) while the summer thresholds are lot closer to the middle of the corresponding concentration distributions. These different statistics can probably explain the corresponding small differences in values. Use of the summer thresholds for winter would produce practically the same results in our analysis. These important points are clarified in the revised paper.

(8) P22270, L9: It is not entirely clear what is meant by "For a fair comparison of volatility distributions for these datasets: : :". Fair in what particular way? It seems to me that these values were, to some extent arbitrarily selected. This is fine, as they are both reasonable. But the "fair" aspect of this selection should be clarified.
We agree with the point of the reviewer and we have deleted the first part of the sentence.

(9) The authors use the terms SVOCs, LVOCs, and ELVOCs in the abstract, yet these are not defined until P22270 and thus any reader unclear with the specific definitions may find their meaning confusing. I suggest the authors be more precise within the abstract.
We have added the definitions of these groups of compounds in the revised abstract.

(10) Figure 3: Returning to the 5 degC bins, I find some of the points presented in this figure to be potentially problematic. The authors report three values (with standard deviations!) for the summer campaign in the range 180-200 degC. However, in looking at Fig. S1, it seems clear that there are only 4 total data points in this region. Thus, I do not think it is at all appropriate to show these points in Fig. 3, and certainly not with error bars as it is entirely unclear where these would have come from. Perhaps there is more data than is shown in Fig. S1, in which case perhaps the

averaging in this range is appropriate, but then the data presentation in Fig. S1 would be misleading. I strongly suggest that the authors change to using at least 10 degC bins (if not even 15 degC).
The error bars in two of the data points in Figure 3 were indeed wrong. We do appreciate the correction. We have updated Figure 3 and these points are shown without error bars. As mentioned above the use of the 10 C bins is reasonable but it does not change the results and the conclusions of the paper. For the points in question it also has almost no effect.

(11) Figure 4 and Figure S3: I believe that Fig. S3 must be moved to the main text. The data need to be shown, not just the results from the data fitting. The readers need to more easily be able to assess the differences between the different thermograms and relate them visually to the bar charts shown in Fig. 4. Additionally, it would seem to me that it is possible for the authors to add error bars (e.g. standard deviations) to each of the MFR points for the factors, as these seem to be the binned values. The data are currently shown in their binned, averaged values, which does not give an indication of the variability associated with the factors themselves. I would strongly encourage the authors to show, for each factor, all of the data points along with their binned values and standard deviations. It would additionally be good if the authors considered both the mean and the median values. Are these similar, indicating a normal distribution? Or do they give very different results? This type of presentation of the data would allow the reader to judge the data quality for themselves. With the data as presented, I can only assume that the variability in each of the thermograms for the different factors is similar to that in the total OA MFR. However, I suspect that the actual variability is a lot greater than for the total. But perhaps it is smaller because the authors have filtered out the low concentration points that may contribute disproportionately to the variability in the total OA MFR values shown in Fig. S1 and S2.
We have followed the suggestion of the referee and added the error bars to each of the MFR points for the factors. The corresponding figure does not add much useful information for the average reader of such a paper. It is mostly for the few specialists who do similar type of data analysis. We believe that it fits better in the Supplementary Material and that Figure 3 provides the important information required by the main paper.

(12) Regarding Fig. 4 itself, I strongly suggest that the authors present the volatility distributions using the same x-axis range for all of the figures. As presented, I find that the reader can easily miss the different scales. (And I do not think that just stating in the caption that the scales are different would be sufficient. The axes ranges should be identical.)
We have followed the reviewer's suggestion and now use the same x-axes for all of the figures.

(13) Regarding the ranges shown in Fig. 4, it becomes clear that the different OA factors were not fit using the same C* range, but instead using an individual range for each one. Otherwise the LV-OOA range is not compatible with the HOA range (for example) if only 6 bins are used. This should be made clear in the text.
We have clarified this point in the revised paper. Different 6-volatility bin solutions were needed for the fitting of the thermograms of the various factors.

(14) The authors state that their volatility distributions have been obtained "using the uncertainty analysis approach of Karnezi et al. (2014)". It is, however, not clear from the presentation whether this includes experimental uncertainty or, more specifically, if it does include

experimental uncertainty how those uncertainty values were established. Standard deviations? See comment above regarding Fig. S3.
We have rephrased this sentence deleting the rather confusing "uncertainty analysis" descriptor. The approach of Karnezi et al. (2014) finds multiple volatility distributions that fit reasonably well the average values of the thermograms and then weighs them to estimate the predicted volatility distribution and its uncertainty. It does not use the experimental uncertainty.

(15) The concentration filtering method of the authors may potentially lead to sampling biases in terms of the time of day of the main measurements. For example, looking at the average diurnal profile for COA in Crippa et al. (2013) for summer COA, the lowest concentrations tend to be found during the day and the highest at night. Thus, the filtering method will oversample nighttime behavior for summer. Although the same general diurnal profile is obtained for COA in winter, the overall concentrations are much larger and thus fewer points are rejected meaning that the time-of-day sampling bias imposed by the filtering criterion will not be as strong. To what extent do the authors believe such differences contribute to the apparent seasonal differences in volatility? Related to this, the average spectra considered for each of the various factors have likely not been weighted to be reflective of the periods excluded from MFR analysis. Thus, the spectra may not be fully representative of the actual chemical composition of the particles for which MFR values were determined. Has this been considered?
This is an interesting point. Our approach implicitly assumes that the AMS spectrum of the factor remains constant during the period of the measurements and that its volatility distribution as a result also does not change. However, there can still be subtle differences that may be hidden. It is very difficult to estimate if there is any bias introduced by our inability to determine the MFR during very low concentration periods. However, we do not believe that this potential bias can explain the significant differences between summer and winter for COA. Our major argument is the observed difference in volatility is consistent with the observed difference in the AMS mass spectra of the factor during the two seasons. Please note that the AMS analysis covers the whole period and no data are excluded.

(16) A comparison with other literature observations is notably absent for the most part. The authors ultimately only compare their derived volatility distribution for one OA factor (BBOA) to the literature. I strongly suggest that the authors compare their work with some of the literature observations that they mentioned in the introduction (p22266). This would facilitate broader understanding of their results.
We have added comparisons with the volatility distributions of Cappa and Jimenez (2010) for Mexico City as well as the few other such studies in the literature.

(17) There seem to be somewhat "standard" colors associated with presentation of AMS factor data in the literature (including in Crippa et al. (2013)). I encourage the authors to utilize this "standard" color scheme to facilitate easier comparison with the literature.
We have done our best with the selection of the colors. Please note that we are also using in Figure 7 different shades to show intensity so we need to be careful to avoid confusion with the use of colors for the various factors.

(18) Figure 6: I suggest that difference spectra might provide easier viewing of the differences in spectra.
We have constructed the corresponding graphs but on their own they are not that helpful. Given that this is not a paper about PMF analysis of AMS results adding two more figures is not worthwhile. We believe that Figure 6 is sufficient for the purposes of this work.

(19) The last line of the abstract should be removed, as it is vague yet, as it turns out, extremely specific.
We have deleted the suggested sentence.

(20) I have some difficulty understanding the specific meaning of statements such as "The summer COA was more than one order of magnitude more volatile than the winter COA" (P22276, L11), given that the authors actually present volatility distributions, not single values. What specifically does it mean to state that a distribution is one order of magnitude more volatile than another distribution? That the highest values are different? That the (weighted) mean behavior is different? The authors should be precise.
We now explain that we are comparing the weighed mean volatility that is also shown in Figure 7 for each factor.

(21) I find the language that the authors "incorporated the results into the 2D-VBS" a bit imprecise. What does it mean to "incorporate" something into the 2D-VBS? My take on what the authors did was to place their derived volatility distributions and measured bulk average O:C ratios onto a particular graph. But I don't see how this information has been "incorporated." Further, the authors should more explicitly recognize the limitation of their placement of their data onto the 2D-VBS framework, specifically that whereas they have volatility distributions they only have bulk average O:C ratios. Thus, they have no information as to how the O:C might have varied within each of the volatility bins for each of the factors. Previous results (e.g. for laboratory SOA, Kostenidou, ES&T, 2009) suggest that the O:C of a factor may vary with temperature, but not necessarily by a substantial amount. Regardless, this limitation should be noted more specifically, especially in the context of statements from the authors such as "These results indicate that there was not a direct link between the average volatility and the average O:C for these OA components." They can say this is the case between factors, but they do not present information that this is true within a given factor.
These are both good points. We have rephrased the sentence and also stressed the limitation of using only the average O:C in this analysis.

Response to Anonymous Referee #2

(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 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.

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.

Volatility of organic aerosol and its components in the Megacity of Paris

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Abstract

Using a mass transfer model and the volatility basis set, we estimate the volatility distribution for the organic aerosol (OA) components during summer and winter in Paris, France as part of the collaborative project MEGAPOLI. The concentrations of the OA components as a function of temperature were measured combining data from a thermodenuder and an aerosol mass spectrometer (AMS) with Positive Matrix Factorization (PMF) analysis. The hydrocarbon-like organic aerosol (HOA) had similar volatility distributions for the summer and winter campaigns with half of the material in the saturation concentration bin of 10 μg m^{-3} and another 35-40% consisting of low and extremely low volatility organic compounds (LVOCs with effective saturation concentrations *C** ~~for bins~~ of 10^{-3}~~, 10^{-2} and~~ 0.1 μg m^{-3} and ~~and~~ ELVOCs *C** less or equal than ~~for bins equal or less than~~, 10^{-4} μg m^{-3}, respectively). The winter cooking OA (COA) was more than an order of magnitude less volatile than the summer COA. The low volatility oxygenated OA (LV-OOA) factor detected in the summer had the lowest volatility of all the derived factors and consisted almost exclusively of ELVOCs. The volatility for the semi-volatile oxygenated OA (SV-OOA) was significantly higher than that of the LV-OOA, containing both semi-volatile organic components (SVOCs with *C**

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in the ~~with bins of~~ 1-~~, 10 and~~ 100 μg m^{-3} range)~~)~~ and LVOCs. The oxygenated OA (OOA) factor in winter consisted of SVOCs (45%), LVOCs (25%) and ELVOCs (30%). The volatility of marine OA (MOA) was higher than that of the other factors containing around 60% SVOCs. The biomass burning OA (BBOA) factor contained components with a wide range of volatilities with significant contributions from both SVOCs (50%) and LVOCs (30%). Finally, combining the bulk average O:C ratios and volatility distributions of the various factors, ~~we locatedincorporated~~ our results are placed into the two-dimensional volatility basis set (2D-VBS) framework. T~~Our results show that t~~he OA factors cover a broad spectrum of volatilities with no direct link between the average volatility and average O:C of the OA components. ~~Agreement between our findings and previous publications is encouraging for our understanding of the evolution of atmospheric OA.~~

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1. Introduction

Atmospheric aerosols have adverse effects on human health (Caiazzo et al., 2013; Pope et al., 2009) and contribute to climate change (IPCC, 2013). Over 50% of the submicron particulate mass is often comprised of organic compounds (Zhang et al., 2007). OA (organic aerosol) originates from many different natural and anthropogenic sources and processes. It can be emitted directly, e.g., from fossil fuels and biomass combustion (so-called primary organic aerosol, POA) or can be formed by atmospheric oxidation of volatile, intermediate volatility and semi-volatile organic compounds (secondary organic aerosol, SOA). Since the oxidation pathways of organic vapors are complex and the corresponding reactions lead to hundreds or even thousands of oxygenated products for each precursor, our understanding of OA formation mechanisms and the OA chemical and physical properties remains incomplete. Furthermore, a lack of information regarding the sources along with the physical and chemical properties, and lifetime of organic aerosol (OA) has made predictions of OA concentrations by chemical transport models uncertain.

The volatility of atmospheric OA is one of its most important physical properties. It determines the partitioning of these organic compounds between the gas and particulate phases, the OA concentration, and the atmospheric fate of the corresponding compounds.

Measurement of the OA volatility distribution has been recognized as one of the major challenges in our efforts to quantify the rates of formation of secondary organic particulate matter (Donahue et al., 2012). Thermodenuders (TD) have been developed to measure the volatility of ambient aerosol (Burtscher et al., 2001; Wehner et al., 2002, 2004; Kalberer et al., 2004; An et al., 2007). Most TDs consist of two basic parts: a heated tube where the more volatile particle components evaporate, leaving less volatile species behind and the denuder tube, ~~containing usually~~usually containing activated carbon where the evaporated material is adsorbed thus avoiding potential re-condensation when the sample is cooled to room temperature. The aerosol mass fraction remaining (MFR) at a given temperature, after passing through the TD, is the most common way of reporting the TD measurements. The MFR, ~~is~~ though an indirect metric of volatility ~~as~~ for a specific TD operation, ~~it depends also~~also depends on the aerosol concentration, size, enthalpy of vaporization, potential resistances to mass transfer, etc (Riipinen et al., 2010).

The two-dimensional volatility basis set (2D-VBS) framework from Donahue et al. (2012) has been used in order to describe atmospheric OA formation and evolution by lumping all organic compounds (with the exception of VOCs) into surrogates along two axes of volatility and the oxygen content (expressed as the O:C ratio or carbon oxidation state). Using the 2D VBS requires the ability to measure the OA distribution as a function of volatility and O:C ratio (or carbon oxidation state).

Positive Matrix Factorization (PMF), aims to deconvolve the bulk OA mass spectra obtained by the aerosol mass spectrometer (AMS) into individual “factors” that give information about the sources or processing of organic aerosol (Lanz et al., 2007; Ulbrich et al., 2009; Huffman et al., 2009; Zhang et al., 2011). Typical factors correspond to either primary sources including HOA (hydrocarbon-like OA), BBOA (biomass burning OA) and COA (cooking OA) or secondary OA like SV-OOA (semi-volatile oxygenated OA) and LV-OOA (low volatility oxygenated OA). Although there have been numerous studies that have identified PMF factors in ambient datasets, there have been few studies that have attempted to estimate the corresponding factor volatility (Huffman et al., 2009; Cappa and Jimenez, 2010). Huffman et al. (2009) characterized the volatility of PMF factors derived for the MILAGRO campaign in Mexico City and for the SOAR-1 campaign in Riverside, CA. They concluded that BBOA was the most volatile and OOA was the least volatile component. HOA was more volatile than OOA in almost all cases. Cappa and Jimenez (2010), using a kinetic evaporation model, estimated the volatility distributions for the various PMF OA factors for the MILAGRO campaign. Here we extend this work focusing on another Megacity, Paris.

In this study, we estimate the volatility distributions of PMF factors derived from two month-long summer and winter campaigns in a suburban background site in Paris. The data analysis approach is first outlined and the corresponding challenges are discussed. We use the mass transfer model of Riipinen et al. (2010), together with the approach introduced by Karnezi et al. (2014) to estimate the volatility distributions for all PMF factors. We finally synthesize the corresponding OA findings using ~~incorporate~~ the ~~results into the~~ 2D-VBS framework ~~synthesizing the corresponding OA findings~~.

2. Methods

2.1 Measurement Site and Sampling

Two comprehensive field campaigns were performed during July of 2009 and January/February of 2010 at an urban background sampling site, SIRTA (Site Instrumental de Recherche par Teledetection Atmospherique) (Haeffelin et al., 2005) located about 20 km southwest of Paris' city center. The datasets were collected as part of a collaborative project known as MEGAPOLI (Megacities: Emissions, urban, regional, and Global Atmospheric POLution and climate effects, and Integrated tools for assessment and mitigation) (Baklanov et al., 2008; Beekmann et al., 2015). A suite of instruments were used including a high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) from Aerodyne research, Inc. (DeCarlo et al., 2006) for particle mass and composition, a scanning mobility particle sizer (SMPS) from TSI, Inc. for particle size and number distributions and the Carnegie Mellon University thermodenuder (TD) for volatility measurements.

The TD design was similar to that described in An et al. (2007), consisting of a heated tube followed by a denuding section, which uses activated charcoal to prevent recondensation of organic vapors. The TD was operated at temperatures ranging from about 20°C to 200°C during both campaigns, yielding thermograms of the organic aerosol mass remaining as a function of TD temperature. The TD scanned this temperature range using different temperatures each day. A centerline residence time of 25 s at 298 K was used for all measurements (Lee et al., 2010). This corresponds to mean residence time of approximately 50 s at 298 K.

Changes in composition, mass, and size as a result of aerosol evaporation were quantified by both the SMPS and the HR-ToF-AMS by alternate sampling between the TD and the ambient sample line, every 5 minutes. The SMPS was operated with a sheath flow of 5 L min^{-1} and a sample flow rate of 0.5 L min^{-1}.~~, extending the size-range of measured particles sizes while maintaining a 10:1 flow ratio.~~ The HR-ToF-AMS, which measures the aerosol size-composition distribution of the submicron non-refractory material, was operated in both the higher sensitivity mode (V-mode) and the higher resolution mode (W-mode) (DeCarlo et al., 2006). The V-mode data are used in this study. The AMS collection efficiency was estimated at 0.38 during the summer (Crippa et al., 2013a) and 0.5 during the winter (Crippa et al., 2013b).

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2.2 Data Analysis

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TD raw measurements need to be corrected for particle losses due to diffusion of small particles, sedimentation of larger particles, and thermophoretic losses (Burtscher et al., 2001). To account for these losses, which depend on particle size, TD temperature, and sample flow rate, Lee (2010) has developed size and temperature dependent corrections for this particular TD. The organic aerosol concentrations measured after the TD ~~mass fraction remaining (MFR) measurements~~ were corrected for losses corresponding to the operating conditions during the campaign. The OA mass fraction remaining (MFR) was calculated dividing the loss-corrected OA concentration after the TD at time period *i* with that of the by-pass line at time period *i*+1. The fact that the two measurements correspond to two different 5 min time intervals introduces some uncertainty in the calculated MFR values because of the variability of the atmospheric concentrations. Some of this variability is averaged out when average MFR values are calculated for each temperature.

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The preparation of these large datasets for analysis required careful examination of the ambient OA variability in order to determine the appropriate averaging intervals. The OA mass concentration data for the summer campaign is shown in Figure 1. Overall, the particulate matter mass concentration was surprisingly low during this period in Paris, with a campaign average PM$_1$ OA for SIRTA of only 0.83 µg m^{-3}. As expected, there were several periods during which the OA concentration was much higher than 1 µg m^{-3} reaching levels up to 6 µg m^{-3}. ~~The collection efficiency due to particle bounce was estimated at 0.385 (Crippa et al., 2013a).~~

To evaluate whether the OA during these higher concentration periods had~~s~~ different ~~behavior~~MFR values ~~volatility~~ than the rest of the samples, we separated the data in two groups using an OA concentration cutoff of 1.5 µg m^{-3}. Figure S1 in the supplementary information shows the corresponding MFR measurements for both low and high concentration periods. Given the experimental variability, there is no discernable difference in evaporation between the higher and the lower concentration periods and therefore, these were averaged together for the analysis. The similarity of the average MFR values during these low and high concentration periods (the latter were often characterized by higher OA variability) also suggests that our calculation of the MFR using measurement pairs did not introduce significant bias in the average estimated MFR.

We performed a similar analysis for the winter campaign. Paris during winter, unlike the summer, was characterized by higher fine PM concentrations with an average PM$_1$ OA concentration of 3.1 µg m^{-3} (Figure 2). The OA threshold concentration was chosen to be 4.5 µg m^{-3} and again there was no evidence of effects of concentration (in the observed range) on volatility (Supplementary Information, Fig. S2) and the corresponding MFRs were averaged together. ~~The collection efficiency due to particle bounce was estimated at 0.5 (Crippa et al., 2013b).~~ Finally, the data points were averaged into temperature bins of 5°C. The calculation of one MFR value every 5^{o}C is a compromise between the need to average more data points at similar temperatures and maintaining the dynamic behavior of the thermogram. Averaging over wider temperature ranges (e.g. 10^{o}C) did not result in any essential differences in our analysis and conclusions.

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Along with the bulk organic measurements, additional information can be derived from the HR-ToF-AMS V-mode mass spectra using the PMF analysis technique. The deconvolved spectra yielded several organic aerosol “factors” for each campaign. A complete discussion of the PMF analysis of the ambient measurements and the resulting factors can be found in Crippa et al. (2013a; b). The PMF analysis was repeated~~performed~~, combining both ambient and thermodenuded spectra with guidance from the original analysis of the ambient-only data (e.g., the same number of factors was used). This second analysis produced ~~The factors derived for this complete dataset (ambient plus TD) were~~ for all practical purposes the same results for the ambient data set as that~~ose~~ of the ambient measurements only and can be found in the corresponding publications.~~.~~

The low OA concentrations especially during the summer resulted in very low concentrations of the corresponding factors and ~~high resulting~~thus high MFR uncertainty. The MFRs of the various factors were, as expected, extremely variable when the factor concentrations were close to zero. Therefore, to minimize these problems, a minimum ambient mass concentration was determined for each PMF factor, based on the concentration range for which ~~several~~ MFR measurements exceeded 1.5~~significantly unity~~. The average ambient concentration and threshold concentration with corresponding statistical information for each PMF factor is shown in Table 1. The corresponding factor concentration thresholds during the summer were in the 0.05-0.1 μg m^{-3} range. MFR measurements of PMF factors with ambient levels less than 0.1 μg m^{-3} are clearly quite uncertain. All the corresponding MFR values from these low factor concentration periods were excluded from the analysis. Few MFR measurements were excluded during the winter period, while 20-50% of the measurements for the various factors were excluded during the summer.

2.3 Volatility Distribution Estimation

To estimate the volatility distributions from the corrected thermograms we employed the dynamic mass transfer model of Riipinen et al. (2010). The model simulates particle evaporation using experimental inputs including TD temperature and residence time, initial particle size, and ambient OA concentration. The volatility of these complex mixtures is defined using the corresponding effective saturation concentration, C^*, at 298 K. Along with saturation concentration, two parameters that can affect the evaporation rate and ~~thus~~ the corresponding volatility estimation are the enthalpy of vaporization and the mass accommodation coefficient. Unfortunately, these values are currently unknown for these complex multi-component systems. Often, a mass accommodation coefficient of unity is assumed. However, mass transfer limitations to evaporation have been observed in some experimental systems, leading to mass accommodation coefficient values of much less than one (Saleh et al., 2013). ~~For a fair comparison of volatility distributions for these datasets,~~ T~~t~~ypical values of 100 kJ mol^{-1} and 1.0 are assumed for the enthalpy of vaporization and accommodation coefficient, respectively.

As described in Donahue et al. (2006), the volatility distribution is represented by surrogate species with a saturation concentration of C_i^*. The C_i^* bins are logarithmically spaced, allowing for extremely low and high volatility species to be compared in a single framework. The analysis here was limited to a 6-consecutive C^* bin solution with a variable mass fraction value for each bin. Different volatility ranges were tested and the best range was selected for each factor. The "goodness of fit" was quantified~~tested~~ using the error analysis outlined in Karnezi et al. (2014). The standard error was calculated for all C^* bin-mass fraction combinations. For a given 6-bin solution, the top 2% of mass fraction combinations with the lowest error was used to find the average mass fraction in each bin and the corresponding standard deviation.

The OA components are described as semi-volatile (SVOCs with C^* of 1, 10, and 100 μg m^{-3}), low volatility (LVOCs with C^* of 10^{-3}, 10^{-2}, and 0.1 μg m^{-3}), and extremely low volatility (ELVOCs with $C^* \leq 10^{-4}$ μg m^{-3}) in the rest of the paper (Murphy et al., 2014).

3. Results and Discussion

3.1 Organic Aerosol Volatility

The average loss-corrected OA thermograms for the two seasons are shown in Figure 3. The two thermograms seem very similar while differences are mostly noticeable at the high temperatures. In the winter thermogram an approximate 30% remained at 180°C while in the summer thermogram less than 10% was present at the same temperature. This might suggest more ELVOCs being present at winter. However, the summer thermogram shows that nearly 50% of the mass evaporated at a thermodenuder temperature of 83 °C (T_{50}). The winter measurements suggested a similar T_{50} value of 88 °C. This crude comparison of volatility through the corresponding thermograms suggests that the OA in the two seasons could have~~d~~ similar average volatility distributions. It is surprising that the seasonal differences in emissions are not reflected in the corresponding thermograms~~volatility measurements~~. We will examine the reasons for this similarity in the subsequent section by analyzing the volatility of the corresponding factors.

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The volatility distributions for the total OA for the two seasons are depicted in Figure 4. They are quite similar to each other especially considering the corresponding uncertainties and they are characterized by higher concentrations of components with $C^*=10^{-4}$ and 10 μg m^{-3}.

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3.2 Volatility of Organic Aerosol Components

Five PMF factors were determined for the summer dataset by Crippa et al. (2013a~~b~~). Hydrocarbon-like OA (HOA) most closely resembles fresh vehicle emissions in that the mass spectrum resembles that of transportation sources. Cooking OA (COA) was also observed in the summer campaign, peaking during noon and evening meal times. Marine OA (MOA) was identified based on relatively high levels of organic sulfur and a strong correlation with methanesulfonic acid (MSA), which is a product of continued oxidation of phytoplankton decomposition products. Two SOA factors were also reported: Semi-volatile oxygenated OA (SV-OOA) and low volatility oxygenated OA (LV-OOA). These two factors were differentiated based on their O:C ratio. The two secondary OA factors made up 57% of the total OA mass. The remaining factors contributed fairly similar average fractions of 18% for COA, 12% for HOA, and 13% for MOA. Detailed discussion of the PMF factors along with verification analysis were provided by Crippa et al. (2013a~~b~~).

The PMF analysis for the winter campaign yielded four factors. The HOA and COA factors were again present. There was also a single secondary OA factor which was termed oxygenated OA (OOA). This factor could not be further separated into SV-OOA and LV-OOA. The final factor reported was biomass burning OA (BBOA), correlating with known molecular markers for residential wood burning (e.g., levoglucosan). The OOA factor was found to dominate the organic aerosol mass, contributing nearly 65% on average. The complete analysis and description of these factors can be found in Crippa et al. (2013b~~a~~).

Using the mass transfer model from Riipinen et al. (2010) and ~~using ~~the ~~uncertainty analysis ~~approach of Karnezi et al. (2014) we fitted the corresponding thermograms (Figure S3), using a C^* bin solution with a variable mass fraction value for each bin. Specifically for each factor we used an individual consecutive 6-bin solution (chosen as the 6-bin solution with the best fits) resulting ~~resulting ~~in the volatility distributions, shown in Figure 5~~4~~. The modeled thermograms for all factors from both summer and winter campaigns are shown in Figure 6~~5~~. Finally, the volatility distributions for each factor are summarized in Table S1 in the supplementary information. The fitting of individual factor thermograms implicitly assumes that each factor had the same size distribution as the total OA and that the factors were present as an external mixture. To test the uncertainty introduced by this assumption we compared the volatility distribution of the total OA with the composition weighted sum of the volatility distributions of the individual OA factors for both summer and winter. The two distributions (total and sum of factors) agreed within a few percent for both seasons suggesting that the uncertainty is modest and within the uncertainty limits shown in the corresponding figures.

The HOA factors for the summer and winter campaigns had very similar thermograms and volatility distributions with half of the material in the 10 μg m^{-3} bin (Figure 5~~4~~). Roughly 40% of the HOA in both seasons consisted of LVOCs and ELVOCs. This volatility similarity is consistent with the similarity in mass spectra derived by the PMF analysis (Figure 7~~6~~a). The angle θ between the corresponding vectors (treating the AMS spectra as vectors according to Kostenidou et al. (2009)) was 14° suggesting similar chemical fingerprints. This is not surprising for a Megacity where the transportation and any industrial sources are expected to have chemically similar emissions in both summer and winter. Similar were also the T_{50} for the HOA factors with values of 49 ^{o}C and 54 ^{o}C for the summer and winter campaign, respectively. Cappa and Jimenez (2010) also estimated that the HOA in Mexico City had a wide volatility distribution with approximately 35% of its mass consisting of LVOCs and ELVOCs while the remaining 65% was SVOCs. Almost 40% of the HOA had $C^* \geq 10$ μg m^{-3} which compares very well with the 50% estimated here.

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The situation was quite different for the cooking OA factor. Here the seasonal differences were more pronounced ~~both~~ for the thermograms (Fig. 6~~5~~), the estimated volatility distributions (Fig. 5~~4~~) and the corresponding mass spectra (Fig. 7~~6~~b). The winter COA was substantially less volatile than the summer COA, more than an order of magnitude based on average logC^* values, weighted by the mass fraction of each bin (average $C^*= 10^{-2}$ μg m^{-3} for the summer campaign and average $C^*= 4\text{x}10^{-4}$ μg m^{-3} for the winter campaign). The COA factor during the winter campaign did not contain semi-volatile components while 37% of the summer COA was semi-volatile. The COA winter factor consisted of ELVOCs (37%) and LVOCs (63%). The COA mass spectra in Figure 7~~6~~b show that the winter COA was characterized by a higher fraction of molecular fragments at higher mass-to-charge (m/z) ratio. This is consistent with organic components of longer carbon chain which, for the same level of oxidation, are expected to have lower volatility. The angle θ between the COA spectra was 26°, suggesting a significant chemical difference. One explanation is that the cooking habits are different in the two seasons with outdoor cooking (e.g., barbecue) dominating in the summer and indoor cooking relying more on oil and butter, being more significant in the winter. We also cannot rule out some imperfect unmixing of OA sources and components. The T_{50} for the COA factors were different as well, with values of 91 ^{o}C and 148 ^{o}C for the summer and winter campaign, respectively.

The LV-OOA factor detected in the summer had the lowest volatility (Fig. 5~~4~~) of all the derived factors. There was no sign of evaporation until the TD temperature reached nearly 150 ^{o}C (Fig.~~ure~~ 6~~5~~). ~~LV-OOA was found nearly non-volatile also in Cappa and Jimenez (2010) from the MILAGRO campaing.~~ We estimate that this factor consisted almost exclusively of OA with effective saturation concentrations equal to or lower than 10^{-3} µg m^{-3}, which are almost exclusively ELVOCs. The average ambient concentration of this factor during the summer was 0.12 µg m^{-3} and its average C^* was equal to $5x10^{-6}$ µg m^{-3}~~µg m^{-3}~~. Very low volatilities (practically all the OA had C* ≤ 10^{-3} µg m^{-3}) were also estimated for LV-OOA by Cappa and Jimenez (2010) in Mexico City during the MILAGRO campaign.

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The estimated volatility for the SV-OOA factor is consistent with its naming by Crippa et al. (2013a) as it was significantly higher than that of the LV-OOA (Fig. 5~~4~~). We estimated that roughly half of the SV-OOA was SVOCs while it contained also LVOCs (42%) and a small amount of ELVOCs (6%). Its T_{50} was 61 ^{o}C and its average C^* was roughly 0.2 µg m^{-3}. These values are once more generally consistent with the estimates of Cappa and Jimenez (2010) showing that SVOCs dominated the SV-OOA during MILAGRO (approximately 40%) with LVOCs contributing another 35%.

The OOA factor determined in the winter had a volatility distribution (Fig. 5~~4~~), containing SVOCs (45%), LVOCs (25%) and ELVOCs (30%). The winter OOA and the summer SV-OOA spectra had a θ angle of 34°, while there was an even larger discrepancy between the winter OOA and the summer LV-OOA with an angle of 37°. The T_{50} was equal to 85^{o}C. These differences in mass spectra and T_{50} are consistent with the differences in volatility. The average volatility of OOA was much higher than LVOOA in summer but lower than SVOOA.

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The marine OA (MOA) factor was only detected during the summer campaign at an average concentration of 0.17 µg m^{-3}. Its volatility was relatively high (Fig. 6~~5~~), and almost all the MOA had evaporated at 100 ^{o}C. The MOA factor consisted mainly of SVOCs (61%) and some LVOCs (36%). Its T_{50} was equal to 58 ^{o}C and its average C^* was approximately 0.4 µg m^{-3}.

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The BBOA factor was present in the winter dataset with an average ambient concentration of 0.6 µg m^{-3}. The corresponding estimated volatility distribution (Fig. 5~~4~~) shows that half of the BBOA factor consisted of SVOCs (with most material in the 10 µg m^{-3} bin) and the other half of LVOCs and ELVOCs. A similar bimodal distribution was also found by May et al. (2013) with a peak at 0.01 and one at 100 µg m^{-3} for controlled biomass burning in the laboratory. The difference in the location of the high volatility peak can ~~probably~~ potentially be explained by the wider range of concentrations in the experiments analyzed by May et al. (2013) compared to the limited range in the ambient Paris measurements. The more volatile BBOA components were never in the particulate phase in our dataset so their abundance cannot be determined. The BBOA T_{50} was 70 °C, higher than that of HOA and less than those of COA and OOA. Finally, its average C^* was approximately 0.1 µg m^{-3}. The BBOA in Mexico City was approximately half LVOCs and half SVOCs (Cappa and Jimenez, 2010) and had a much lower ELVOC fraction than the wintertime Paris BBOA in the present study. ~~Differences for BBOA factor are also found in Cappa and Jimenez (2010), where BBOA factor was found to be the most volatile factor followed by the factor of HOA and SV-OOA.~~

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4. Synthesis of Results in the 2D-VBS

We employed the 2-D VBS framework in order to synthesize the above results, combining the bulk average O:C ratio and volatility distributions of the various factors. Each of the different factors had ~~obviously~~ a distribution of O:C values, but this distribution cannot be determined from the AMS measurements. The HOA, BBOA, and COA factors ~~had~~ all had relatively low O:C values but they covered a wide range of average volatilities (Fig. 8~~7~~). The MOA and secondary OA factors for both seasons had much higher O:C values but they also covered a wide range of volatilities, with LV-OOA having the lowest one. The HOA during summer~~,~~ had higher O:C than HOA during winter, suggesting incomplete separation from aged HOA or difference in the sources, while their volatility distribution was similar, as discussed earlier. The COA factor during the summer campaign, had slightly higher O:C and a higher volatility than the COA from the winter campaign. The OOA during the winter had the highest O:C ratio but ~~also~~ compared to the less oxidized SVOOA, it had lower average volatility and higher volatility compared to LVOOA. These results indicate that there was not a direct link between the average volatility and the bulk average O:C for these OA components. This is actually the reason for the introduction of the 2D-VBS: the second dimension is needed to capture at least some of the chemical complexity of the multitude of organic compounds in atmospheric particulate matter.

The broad spectrum of volatilities and extent of oxidation are not surprising. Donahue et al. (2012) extrapolated from the few available ambient measurements to provide rough estimates of the factor locations on the 2D-VBS. Superimposition of our factors and those estimated by Donahue et al. (2012) (Fig S4) indicates that the factor locations agree surprisingly well. This is quite encouraging both for our results and our current understanding of the evolution of atmospheric OA.

5. Conclusions

Two month-long field campaigns were conducted at an urban background sampling site, SIRTA in Paris, France as part of the collaborative project MEGAPOLI. The particulate matter mass concentration was surprisingly low during summer in Paris, with a campaign average PM_1 OA for SIRTA of only 0.83 μg m^{-3}, while during winter it was characterized by higher fine PM concentrations, with an average PM_1 OA concentration of 3.1 μg m^{-3}.

The volatility distributions of PMF factors derived during both campaigns were estimated. Five factors were determined for the summer dataset. Hydrocarbon-like OA (HOA), cooking OA (COA), marine OA (MOA) and two Secondary OA (SOA) factors were also identified: Semi-volatile oxygenated OA (SV-OOA) and low volatility oxygenated OA (LV-OOA). The PMF analysis for the winter campaign determined four factors. The HOA and COA factors were again identified. There was also a single secondary OA factor that was termed oxygenated OA (OOA). The final factor observed was biomass burning OA (BBOA).

The HOA factors for both campaigns had similar volatility distributions with half material in the 10 μg m^{-3} bin. Both factors contained also LVOCs and ELVOCs with a total contribution of around 40% to the HOA mass. This similarity was consistent with the corresponding mass spectra derived by the PMF analysis.

The summer COA was significantly ~~more than one order of magnitude~~ more volatile than the winter COA. The weighted-average COA C^* during the summer was more than order of magnitude higher than that in the winter. The winter COA did not contain any semi-volatile organic components (SVOCs) whereas 37% of the summer COA was semi-volatile. LVOCs were significant components of the COA, representing 37% of the COA in the summer and 63% in the winter. These differences in volatility were consistent with the differences in AMS spectra and could be due to different seasonal cooking habits. Also, imperfect separation of the OA components by PMF cannot be excluded.

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The LV-OOA factor detected in the summer had the lowest volatility of all the derived factors. There was no sign of LV-OOA evaporation until the TD temperature reached 150 ^{o}C. The LV-OOA factor consisted ~~practically~~ nearly exclusively of ELVOCs (97%). Roughly half of the SV-OOA mass consisted of SVOCs while the rest was mainly LVOCs (42%). The OOA factor determined in the winter had a volatility distribution~~,~~ containing SVOCs (45%), ELVOCs (30%) and LVOCs (25%).

The marine OA (MOA) factor, only detected during the summer campaign, was relatively volatile with an average C^* of approximately 0.4 μg m^{-3}. The MOA factor consisted mainly of SVOCs (61%) and LVOCs (36%).

The BBOA factor was present in winter with an average ambient concentration of 0.6 μg m^{-3}. Half of the BBOA consisted of SVOCs and the other half of extremely low volatile and low volatile organic components. The BBOA was less volatile than the HOA factors but more volatile than COA and OOA.

Finally, combining the O:C ratio and volatility distributions of the various factors, we ~~placed our~~integrated our ~~incorporated the~~ results into the 2D-VBS synthesizing the corresponding OA findings. The factor locations agreed well with the location of factors proposed by Donahue et al. (2012). The HOA, BBOA, and COA factors had all relatively low O:C but their average volatilities were different by orders of magnitude. The MOA for summer and secondary OA factors for both seasons had much higher O:C with a wide variety of volatilities, where MOA had the highest one and LV-OOA had the lowest one. The results suggest that the average O:C factor was not directly linked to its average volatility, underlining the importance of measuring both properties, and that all factors include compounds with a wide range of volatilities.

The estimated volatility distributions by the use of just TD measurements are characterized by considerable uncertainties (Karnezi et al., 2014). However, the relative volatilities of the various factors discussed above should be ~~a lot~~ more robust. The absolute volatility distributions do depend on the assumed enthalpy of vaporization and accommodation coefficient (parameterization of mass transfer resistances). They also depend on the assumptions of similar size distributions and external mixing of the OA components corresponding to each factor.

Acknowledgements

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Table 1. Average and threshold ambient concentrations for each PMF factor.

PMF Factor	**Season**	**Average Mass Concentration** (μg m^{-3})	**Threshold Concentration** (μg m^{-3})	**Percentage of Measurements above Threshold**
HOA	Summer	0.16	0.08	53
COA		0.25	0.05	69
MOA		0.17	0.10	73
SV-OOA		0.65	0.10	82
LV-OOA		0.12	0.08	69
HOA	Winter	0.95	0.20	95
COA		0.48	0.08	92
BBOA		0.60	0.07	90
OOA		3.78	0.40	99

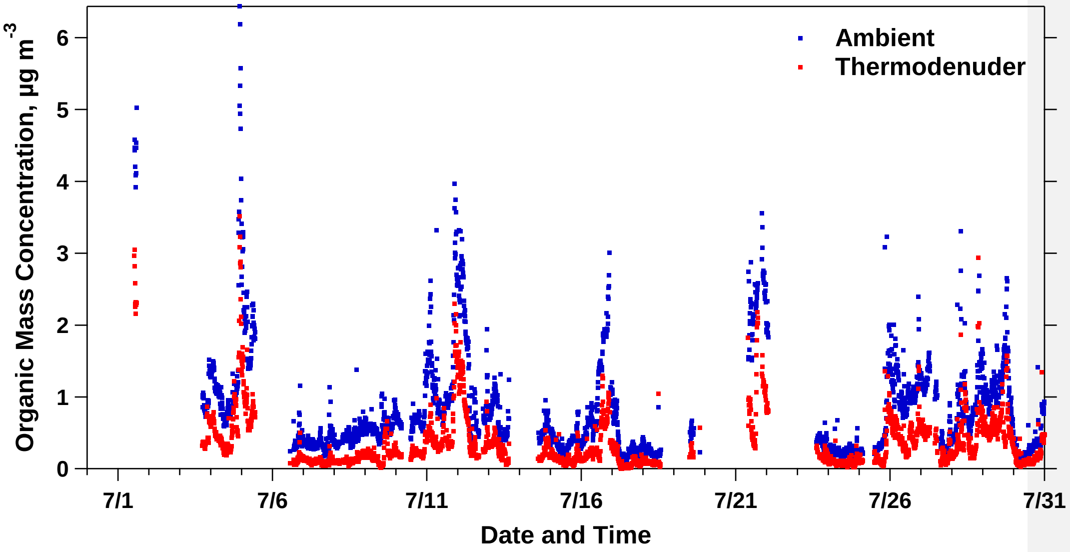


Figure 1. Ambient (blue dots) and thermodenuder (red dots) organic mass concentration measurements for Paris during summer 2009.

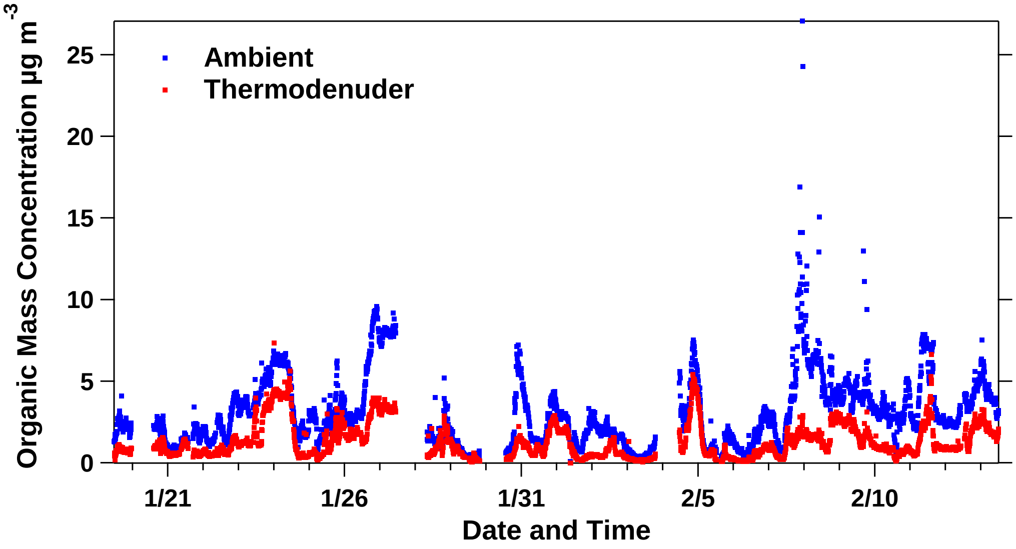
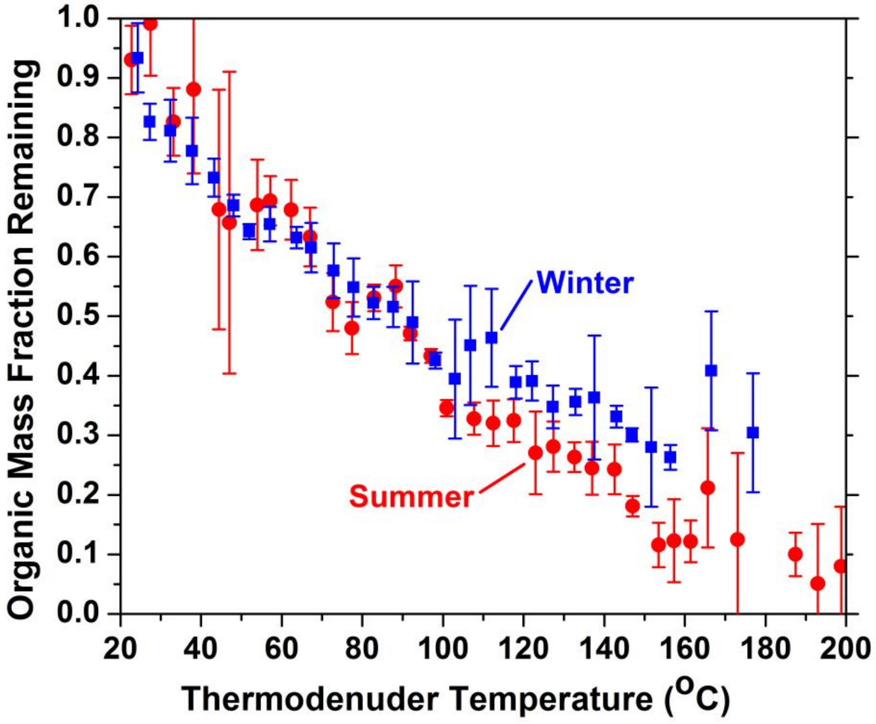


Figure 2. Ambient (blue dots) and thermodenuder (red dots) OA mass time series for the winter 2010 campaign.


Organic Mass Fraction Remaining
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
20
40
60
80
100
120
140
160
180
200
Thermodenuder Temperature (^{O}C)
Winter
Summer

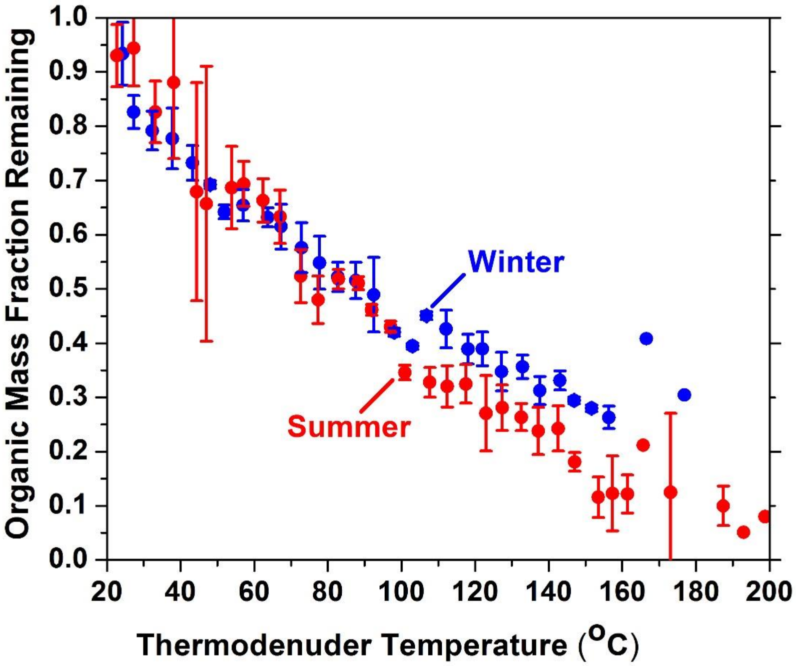


Figure 3. Loss-corrected average OA thermograms for summer (red circles) and winter (blue squares) campaigns. The error bars correspond to plus/minus 2 standard deviations of the mean. Points with no error bars correspond to a single measurement.

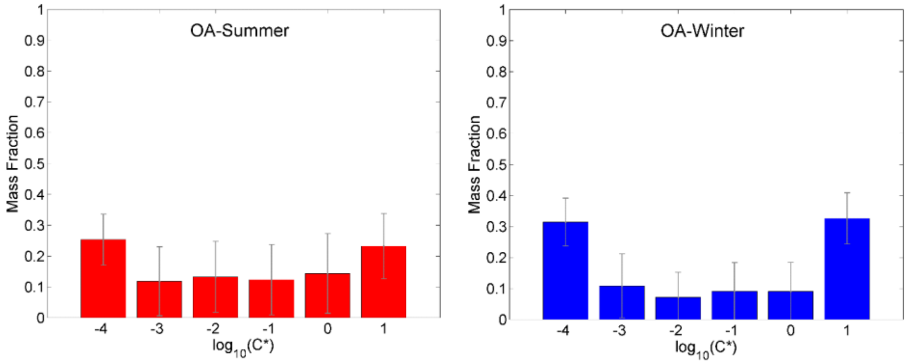


Figure 4. Estimated volatility distributions for summer (left panel) and winter total OA (right panel). The error bars correspond to the fitting uncertainties according to the algorithm of Karnezi et al. (2014).

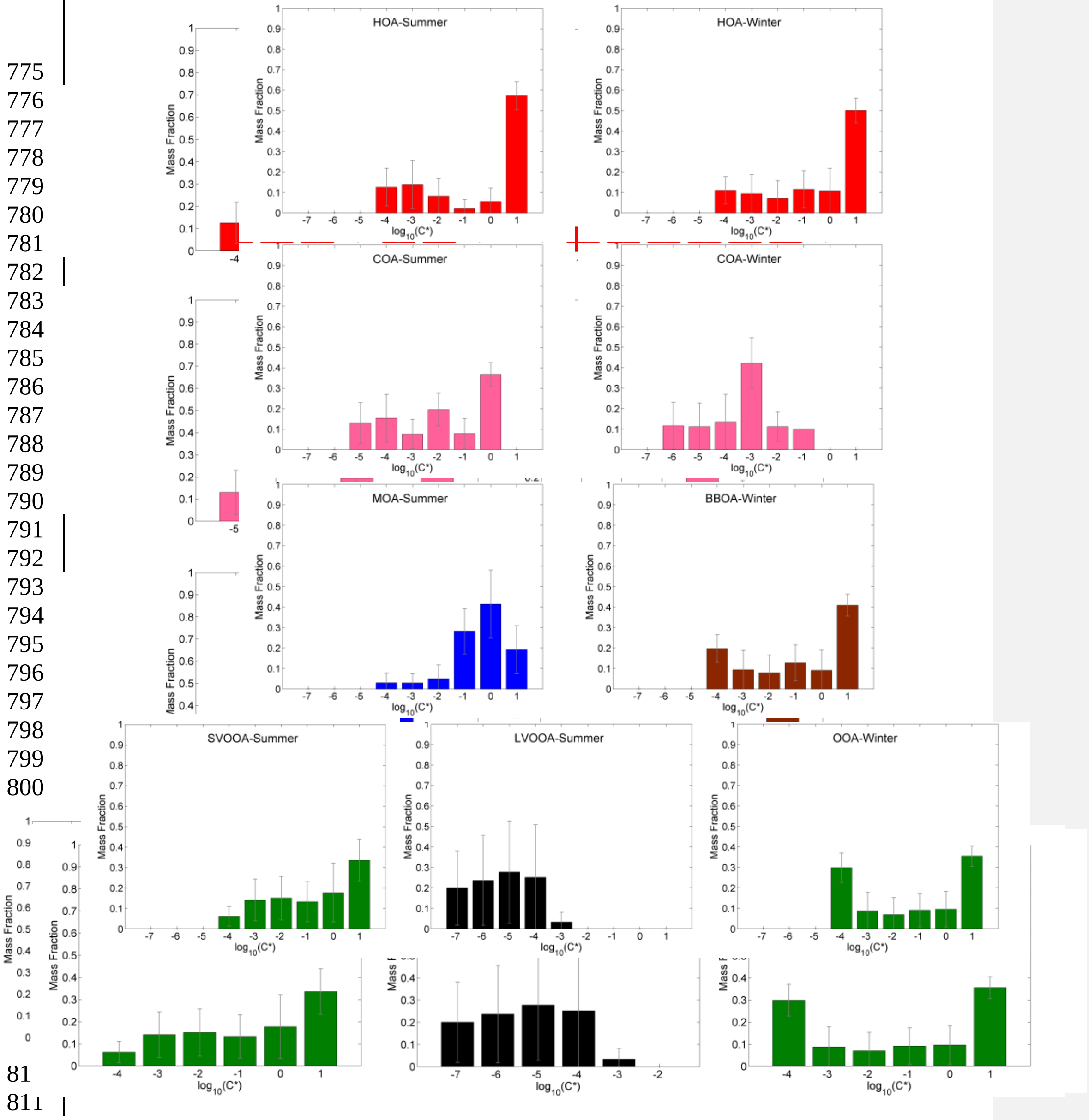


Figure 54. Estimated volatility distributions for summer PMF factors (left panel) and winter PMF factors (right panel). The error bars correspond to the fitting uncertainties according to the algorithm of Karnezi et al. (2014).

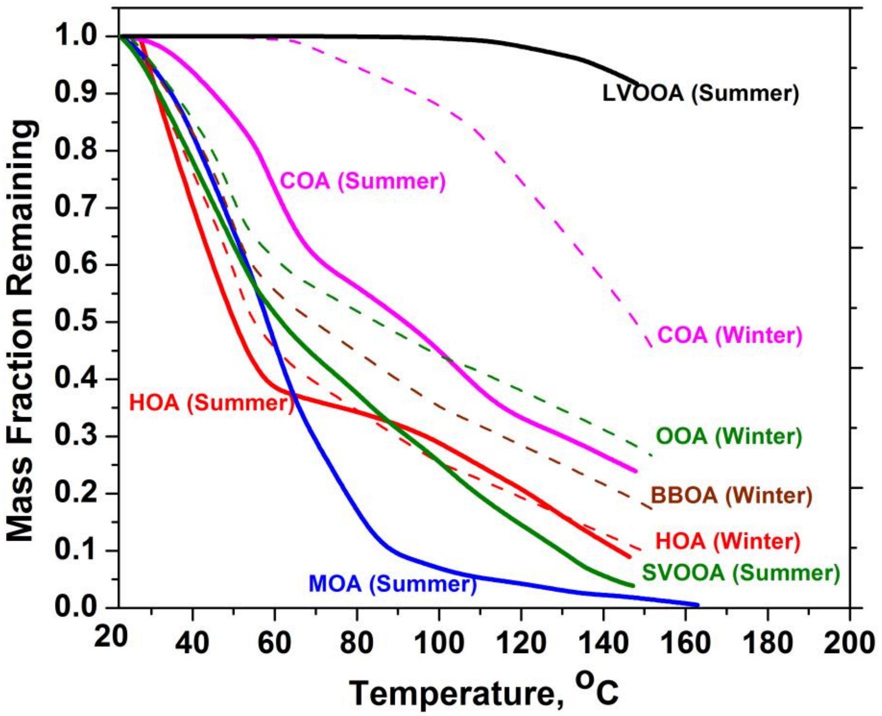


Figure 6~~5~~. Estimated best-fit thermograms for all PMF factors. The solid lines represent the thermograms for the summer campaign and the dashed lines the thermograms for the winter campaign.

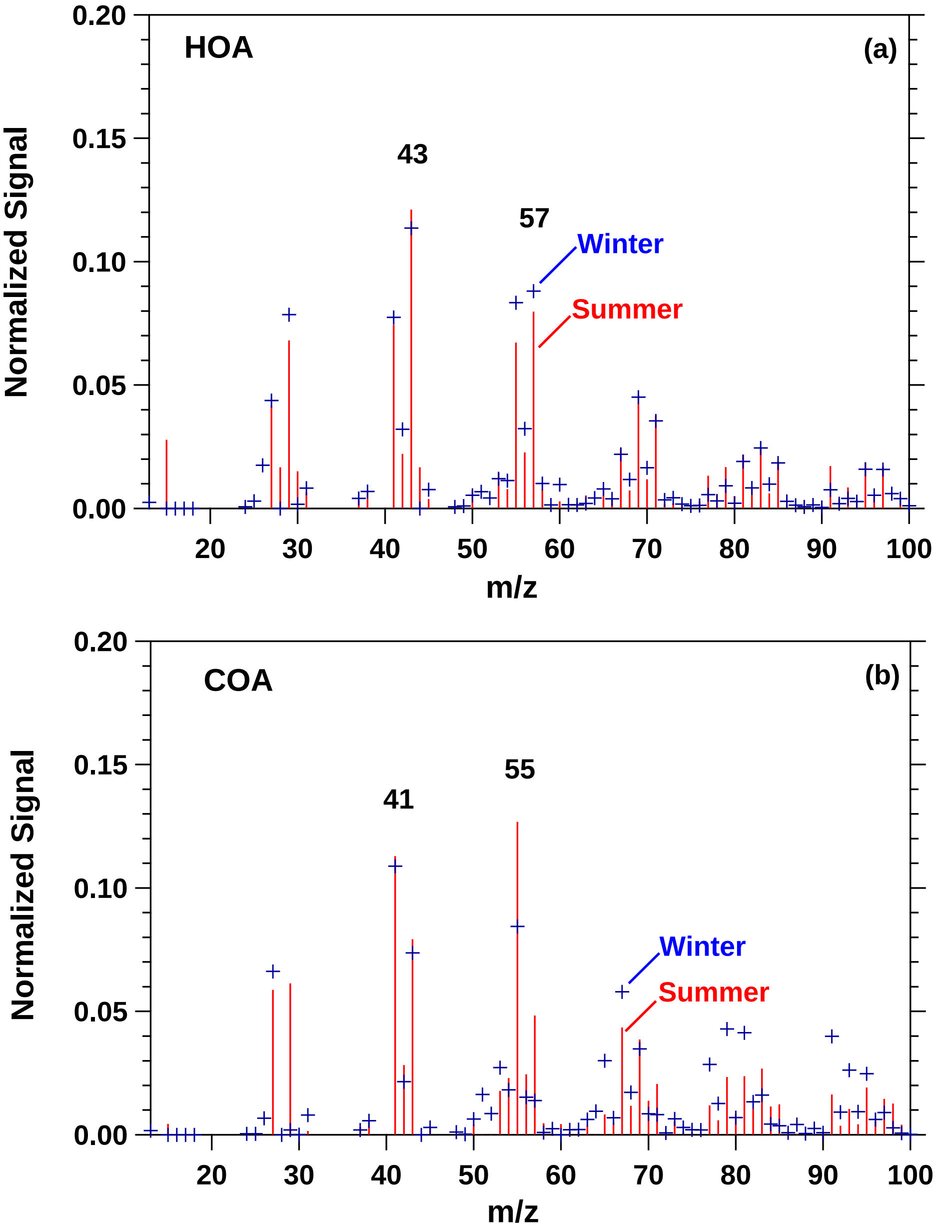

(a)
HOA
Normalized Signal
0.20
0.15
0.10
0.05
0.00
43
57
Winter
Summer
20
30
40
50
60
70
80
90
100
m/z
(b)
COA
Normalized Signal
0.20
0.15
0.10
0.05
0.00
41
55
Winter
Summer
20
30
40
50
60
70
80
90
100
m/z

Figure 7~~6~~. Seasonal mass spectra comparison for (a) HOA and (b) COA in Paris. Red lines correspond to the summer measurements while blue symbols correspond to the winter data.

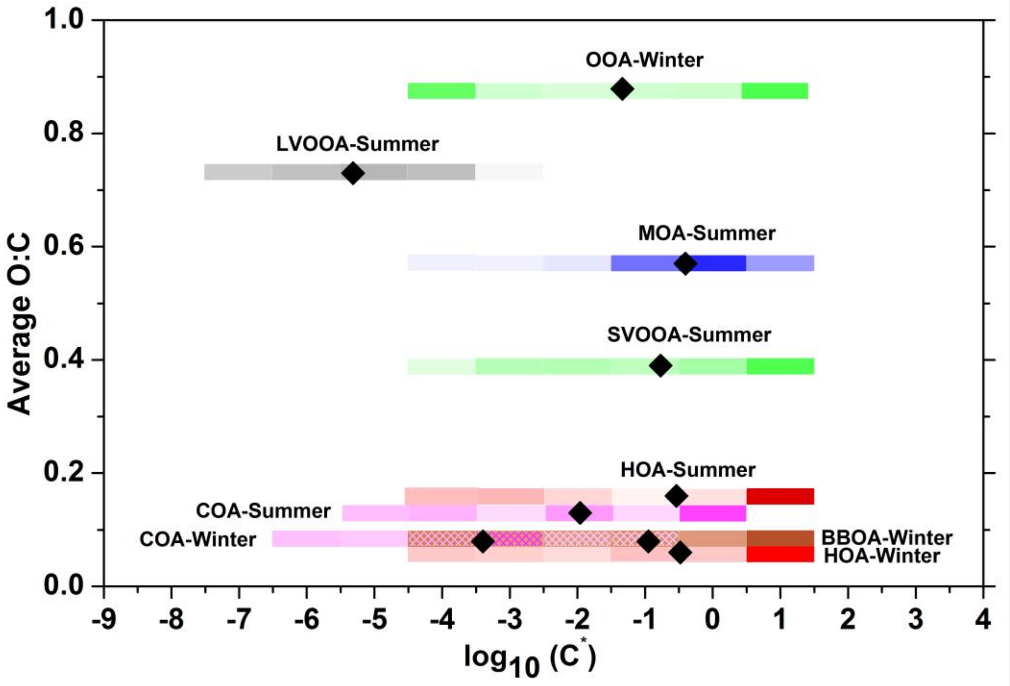


Figure 8~~7~~. 2-D VBS representation of the PMF factors for the summer and winter campaigns. With the red color of the bars we represent the HOA factors, with the pink color the COA factors, the green the SVOOA and OOA, the blue is for the MOA factor, the brown for the BBOA factor and the black for the LVOOA factor. The darker shading of the colored bars denotes a larger mass fraction for a given C^* bin. The diamond represents the average $\log_{10}(C^*)$ value for a given PMF factor.