Responses to the Comments of Reviewer 1

(1) Drosatou et al. present a study in which chemical transport model predictions of organic aerosol over Europe are used in a PMF (and ME-2) analysis to determine what types of organic aerosol factors exist in model predictions. The use of a chemical transport model means that the PMF factors can be directly examined in terms of their sources and identity. The major findings include the composition of POA factors in terms of potential SOA contributions and expected error as well as identification of 2 types of SOA or OOA-like factors in a variety of locations. They show that the two types of SOA do not separate anthropogenic and biogenic SOA and the separation is mainly based on age. This is a useful analysis and comments below focus on two main areas.
We appreciate the comments and suggestions of the reviewer. Our responses and corresponding changes in the manuscript (in black) can be found below after each comment (in blue).

Main comments:

Methodology

(2) How would results be different if source information (for example the chemical identity of POA and bbPOA) was not used in the PMF analysis of model output? If the volatility of the model-predicted OA was the only chemical information in the PMF analysis, would you get similar results? This may provide insight into how results from this work translate to AMS analysis in which sources may not be very chemically distinct due to fragmentation.
This is an interesting suggestion allowing the PMF to focus just on the volatility of the OA. We have repeated the PMF analysis using only the volatility distributions. We first tried two factors. The corresponding PMF factors included material from all volatility bins. So PMF did not separate the OA into semi-volatile and low volatility material. In the next step we assumed three factors but still the factors included surrogate compounds with a mixture of volatilities. We have added a new sub-section in the Results to discuss the results of this test simulation that further supports our conclusion that PMF does not separate OA components solely based on their volatility.

(3) PMF appears to have been performed on a site by site basis. Can this be clarified? The analysis generally always leads to two SOA (or OOA) factors, but the composition of the SOA factors varies by site. How many SOA factors would be obtained if all locations from the model were used in one PMF analysis? An analysis along these lines could help inform questions in the second main comment regarding how different the two OOA factors are in different locations or studies.
Indeed, the analysis presented in the original paper was performed for each site separately similarly to the analysis of field campaign measurements. This is now clarified in the manuscript. We have followed the reviewer’s suggestion and performed an additional test in which we combined results from all seven sites (all the examined areas in the paper). The application of PMF to this comprehensive set resulted in four factors: fresh biomass burning, other primary OA and two secondary OA factors (fresh and aged SOA). The number and character of the factors were similar with the site by site analysis,

but there were differences in the composition and contribution of the factors. The results of this test are now discussed in the revised paper.

(4) What information is introduced by the PMF analysis of model output that is not otherwise available? Could the same “factors” be obtained by determining how much POA, SOA-sv, bSOA, aSOA, etc correlate or covary and making two groups?
The reviewer is correct; factor analysis methods are in general based on the temporal correlation among the concentrations of different pollutants. However, in their effort to limit the dimensionality of the chemical (or AMS m/z) space, these approaches distribute the pollutants into factors in ways that are by no means transparent. Our goal in this work has been to shed a little more light on what PMF does when it is applied to the AMS organic aerosol data. We have added this brief discussion in the paper.

(5) How was the boundary condition OA at the edge of the domain specified and evaluated? If the boundary OA was not assigned a C* of 0.01 ug/m3, would it have ended up in a different factor?
In general boundary conditions of regional chemical transport models are obtained from the output of similar global models or from some averages of measurements. For the purposes of this work we assumed low volatility constant OA boundary conditions. This choice facilitates the separation of highly aged OA coming from outside the modeling domain from the fresher material that is emitted and/or produced inside the domain. Obviously, the absolute OA concentrations especially near the boundaries of the domain can be dominated by these boundary conditions. To avoid such issues, we have used sites that are far from the boundaries. Overall, our conclusions are quite robust to the choice of the OA boundary condition values.
The effect of our choices of OA boundary conditions is now discussed in the paper.

(6) Meaning of two SOA or OOA factors. Is the proliferation of terms in literature (LO/MO-OOA, OOA-1/2, LV/SV-OOA) indicating true site to site variability in the OOA components or is it just a nomenclature choice?
We believe that the evolution of the terms used to describe these two factors reflects our understanding (or lack there-of) of the nature of these factors and not so much site to site variability. The use of OOA1 and OOA2 reflected the complete lack of understanding. Then the use of Less and More Volatile OOA showed the beginning of some understanding, but it has probably led to some confusion and a few misconceptions. The next step (use of Less and More Oxidized OA) is probably more accurate. Our work here supports the hypothesis that these factors correspond to Less and More Aged OOA present in each site. We have added this discussion to the corresponding section of the paper.

(7) The authors argue that the designation of the two AMS factors based on volatility is somewhat misleading due to overlap in their volatility. I was not convinced that this designation was misleading (based on Figure 10) but do agree that it is a simplification. What is the best description of the two factors given that they likely overlap on many metrics (volatility, O:C, age, etc) and age, O:C, and volatility covary?
The use of the volatility-based terminology suggested to most of us that there is a volatility threshold and OA components that are more volatile than this are grouped by

PMF in one factor (e.g., SV-OOA) and the less volatile compounds in the second (LV-OOA). Our results both from this theoretical analysis but also from direct volatility measurements of AMS factors (Paciga et al., 2016; Louvaris et al., 2017) suggest that this is not the case. The so-called semivolatile factor may include very low volatility OA and vice versa the so-called low-volatility factor may include semivolatile material. We believe that the use of more and less oxygenated is safer and that the use of more and less aged will be probably proven to be more accurate.

(8) How should CTMs evaluate their predictions compared to AMS data beyond SOA vs OOA? Can the analysis here be used to provide a range of agreement where models can be assumed "in agreement?"
This is an excellent question. Our results suggest that the comparison of CTM predictions of POA and fresh biomass burning OA to the corresponding AMS results is meaningful if these are major sources and taking into account the uncertainties estimated here. The comparison of the less and more volatile OA predicted by CTMs to the corresponding OOA factors is probably not a good idea. Summation of the two OOA factors into just OOA appears to be quite safe based on our results here. On the other hand, if a CTM can keep track of the age of OA the comparison of more and less aged predicted OA to the two OOA factors could be potentially useful. We have added this discussion about model evaluation to the paper.

Minor comments:

(9) Lines 22-28 of the abstract are useful, but could be condensed. Mentioning the fraction of the POA factor that is secondary (e.g. lines 477-478) would be even more useful.
We have followed the reviewer's suggestion and rewrote this part of the abstract.

(10) Lines 81-104 are missing the MO- and LO-OOA designations (Xu et al. 2015 PNAS https://doi.org/10.1073/pnas.1417609112) in the discussion and how those fit with the other AMS PMF factors from literature.
We have tried to keep the terminology used in the corresponding studies to both show the evolution of the nomenclature but also the rather confusing picture. We have added a sentence indicating the correspondence of the terms (for example OOA-1, LV-OOA and MO-OOA have been used for the same factor in most studies).

(11) Line 134: what version of SAPRC was used?
A version of SAPRC99 extended to include the VBS species was used in this work. This information has been added to the text.

(12) Paragraph starting at line 250: Clarify that there was no observed POA or bbPOA factor in observations or model for Melpitz.
We have added this clarification in the revised paper.

(13) Figure 3: Could boundary OA and POA+S/IVOC-SOA be added to panel (b)? Could SOA (excluding boundary and S/IVOC-SOA) be added to panel (a)? How much

value does the PMF factor bring compared to classifying boundary and S/IVOC-SOA as one type and all other SOA as one type?
The major point of this figure and the corresponding example of the PMF analysis in Melpitz is that the analysis of the ambient AMS dataset and that of the PMCAMx VBS predictions results in the same number of factors with a very similar diurnally-averaged behavior. This supports our hypothesis that the PMF analysis of the PMCAMx predictions can help us understand better the results of the PMF/AMS analysis. One can try different combinations of the predictions of PMCAMx and compare them to the results of PMF/AMS (see for example Fountoukis et al., 2014 for such an effort), but this is outside the scope of this work. Please note that we are not suggesting that PMF should be applied to CTM results. CTMs (as we show in this work too) provide directly information about sources of OA without the need of PMF. A brief discussion of this point has been added.

(14) Figure 7: How were the locations chosen?
We have added a description of our criteria for the choice of these locations. Briefly, Majkow Duzy (Poland) has the highest predicted contribution of POA to OA. St. Petersburg, Catania and Majden are three locations in different environments with bbOA during the simulation period. Melpitz, Cabauw and Finokalia were chosen because there are AMS measurements available for the simulation period and they also cover quite different environments. The other sites in Figure 7 were chosen because they had different predicted bbOA/levels and they could help us get information for the full range of values.

(15) Figure 7: What would you expect the NME to be for typical urban, suburban, or rural conditions (add to plot)?
Based on our analysis the actual contribution of bbOA to the total OA is more important than the type of environment for Europe at least. If a site (even if it is urban) is influenced by a major nearby fire contributing significantly to the OA then PMF does well in quantifying its impact. If on the other hand if a rural site is only marginally affected by far away fires then the corresponding normalized error can be significant.

(16) Did the model include any aqueous SOA? Where would that appear in the PMF analysis?
No, this version of PMCAM did not include aqueous SOA production. The treatment by PMF of such OA that has been produced by a different pathway is an interesting question for future work.

Editorial comments

(17) Line 126: "a regional three-dimensional CTM" is duplicated within the sentence.
We have rewritten this sentence.

(18) Figure 1: Needs (a) and (b) labels or titles.
We have added the corresponding labels.

(19) Figure 2: Could be on same panel in different colors.

We would prefer to keep them separate. The figure becomes rather confusing when these two timeseries are in the same panel.

(20) Figure 4: Could go in SI.
We have followed the reviewer's suggestion and moved this figure to the SI.

(21) Figure 11: switch columns 3 and 4 so that both Melpitz and Finokalia data reads as increasing age going left to right.
We have switched the order of the two Finokalia factors for consistency with the Melpitz factors.

Responses to the Comments of Reviewer 2

(1) This paper summarizes PMF analysis conducted on OA simulated from a chemical transport model and compared with AMS PMF factors for a single summer month. The authors find similar number and categorization of PMF factors as AMS, and provides further insight for the modeled factors. First, the primary (HOA-like) factor often contains some SOA and biomass OA. Second, two OOA components found are likely more oxygenated and less oxygenated, but are not always separated in volatility space. Finally (among other conclusions), SOA from various sources can be lumped into a single PMF factor. The manuscript is well-written and easy-to-read. Many of the technical decisions (e.g., regarding the PMF error matrix for simulations) seem well justified, and there are additional insights regarding errors in source apportionment (mixing of sources or not extracting the source altogether) during periods of minor contributions. These results are of great interest to the atmospheric chemistry community and is therefore recommended for publication with minor revisions.
We appreciate the positive assessment of our work. Our responses and corresponding changes in the manuscript (in black) can be found below after each comment (in blue).

General comments:

(2) The authors do not seem to explicitly mention this, but PMF appears to have been conducted separately at each site. One reason for applying site-specific PMF to measurements is that anthropogenic or biogenic SOA can be different at each site, but in these simulations they are effectively the same (e.g., a lumped species with C* belonging to anthropogenic POA is chemically the same across sites). However, the site-specific PMF is still desirable here for capturing site-specific proportion of source classes in each factor, and for comparison with site-specific AMS PMF?
This is a good point also made by the first reviewer (Comment 3). Indeed, the PMF analysis presented in the original paper was performed for each site separately similarly to the standard analysis of field campaign measurements. This is now clarified in the manuscript.

We have complemented this site-by-site analysis with analysis of the combined data in all sites. The application of PMF to this comprehensive set resulted in four factors: fresh biomass burning, other primary OA and two secondary OA factors (fresh and aged SOA). These could explain well the overall dataset. The number and character of the factors were similar with the site by site analysis, but there were differences in the composition and contribution of the factors. The results of this test are now discussed in a new section in the revised paper.

(3) The assumption that the components are "chemically different" is mentioned a couple of times, but it is not further discussed. For instance, the lumped species differ in C* or reactivity with OH (depending on source class) so in many cases they are already treated as being chemically different. For the remaining lumped species, it’s not unlikely that species from different source classes grouped in the same bin C* are likely structurally different. However, a real chemical difference with respect to gross properties should not

necessarily be required by PMF either, as it is possible to use isotope-labeled compounds in the analysis (which source-tagging effectively does here).
This is an important aspect of our analysis that needs further clarification because it is the most important difference of our CTM-based approach and the AMS/PMF analysis of field data. As we provide PMF with the concentrations of 27 different predicted OA surrogate components, we implicitly assume that the corresponding measurement technique or techniques can separate and quantify these components. For the AMS, this may not be the case as two OA components (e.g., processed bbOA and aged SOA) may have quite similar AMS spectra. Of course, other measurement techniques, like the one mentioned by the reviewer, have different capabilities. We now provide a little more discussion about this assumption underlying our work.

(4) Is the simulated OA size fraction used for PMF analysis equivalent to PM2.5 or what might be more directly comparable to the submicron fraction measured by AMS?
We have used PM_1 for our analysis for consistency with the AMS measurements. However, the difference in predicted OA in the PM2.5 and PM1 range is small in PMCAMx so our conclusions are also valid for PM2.5. This point is now explained in the revised paper.

(5) Can the authors remark on the fact that the model, which does not include aqueous phase or condensed-phase chemistry, generates factors which agree on a "high-level" with AMS factors? Is it that condensed-phase processes do not provide sufficient differentiation from covariations fixed by vapor-phase processes? Or could it a limitation of the sites/period studied?
This is a very interesting question also posed by the first reviewer (Comment 16). One could speculate that it may grouped by PMF together with the other aged OA. Unfortunately, we cannot test this hypothesis with the results of the current version of the model that does not include aqueous-phase production of SOA. It is clearly a good topic for future work.

(6) The authors have previously published work integrating 2D-VBS into PMCAMx in the European domain; the model used here is apparently different and referred to as PMCAMx-SR - but the citation refers to a manuscript in preparation so it is hard to understand some of the details. How is this model different and why was the 1-D VBS selected? For this comparison with AMS, comparison of O/C ratios would have been useful to show further correspondence (or differences) between simulated and measured PMF factors (e.g., Aiken et al. 2008, Canagarathna et al. 2015); the authors may wish to add justification for the decision they made here.
The reviewer is correct, the version of the model used here (PMCAMx-SR) is based on the 1D-VBS, similarly to the regular PMCAMx. Its major difference from its sister model is its ability to simulate separately the primary and secondary OA from different sources. Therefore, one can use different volatility distributions and aging schemes for organic compounds from different sources. This allows us in this work to use more up-to-date information about the bbOA properties. Use of the OA from the 2D-VBS in a similar exercise is in an excellent idea and could allow one to include the O/C in the analysis. This is the topic of ongoing work.

(7) Others have found instances where the low/high volatility designation of PMF OOA do apply (e.g., Cappa and Jimenez 2010), so the conclusion (line. 512) that the nomenclature is misleading seems to broad - it may be rephrased that statistical separation of OOA by volatility cannot always be assumed?
The use of the volatility-based terminology suggests that there is a volatility threshold and OA components that are more volatile than this are grouped by PMF in one factor (e.g., SV-OOA) and the less volatile compounds in the second (LV-OOA). Our results both from this theoretical analysis but also from direct volatility measurements of AMS factors (Paciga et al., 2016; Louvaris et al., 2017) suggest that this is not the case. The so-called semivolatile factor may include very low volatility OA and vice versa the so-called low-volatility factor may include semivolatile material. We have rephrased the statement to indicate that it may be misleading in at least some cases.

Minor comments

(8) Should the acronym PMCAMx be defined? For instance, CMAQ (Community Multiscale Air Quality Modeling System) is typically spelled out when first introduced in a paper.
We have added the definition of the acronym PMCAMx (Particulate Matter Comprehensive Air Quality Model with extensions).

(9) Regarding terminology, line 141: "primary organic compounds are all considered to be semi-volatile with C* ranging from 10ˆ-2 to 10ˆ6 microg/mˆ3" whereas Donahue, Robinson, and Pandis (2009) define SVOCs to have C* ranging between 10ˆ0 and 10ˆ2 microg/mˆ3.
We have rephrased this sentence that may confuse some readers about the definition of the term “semi-volatile”.

(10) Figure 7: Is this not more a reflection of the deviation in source apportionment for both measurements and simulation when the source contribution becomes small, rather than error that can be purely attributed to the apportionment from the simulation side (as reflected by normalization to observed values)? Section 3.4 should correspondingly be renamed since "PMF error" can imply many things (error matrix, residual matrix, etc.).
The reviewer is right in general, however in our case the “measurement” error is zero as we use predicted values as inputs to the PMF algorithm. So this error is all due to the source apportionment algorithm. Our analysis suggests that this can be quite significant (a factor or 2 or more) for the smaller OA sources, so the corresponding estimates should be used with caution. We have changed the title of Section 3.4 to “PMF source apportionment error”.

Positive Matrix Factorization of Organic Aerosol: Insights from a Chemical Transport Model

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Abstract

Factor analysis of Aerosol Mass Spectrometer measurements (organic aerosol mass spectra) is often used to determine the sources of organic aerosol (OA). In this study we aim to gain insights regarding the ability of positive matrix factorization (PMF) to identify and quantify the OA sources accurately. We performed PMF and multilinear engine (ME-2) analysis on the predictions of a state-of-the-art chemical transport model (PMCAMx-SR, Particulate Matter Comprehensive Air Quality Model with extensions-Source Resolved) during a photochemically active period for specific sites in Europe in an effort to interpret the diverse factors usually identified by PMF analysis of field measurements. Our analysis used the predicted concentrations of 27 OA components, assuming that each of them is "chemically different" from the others.

The PMF results based on the chemical transport model predictions are quite consistent (same number of factors and source types) with those of the analysis of AMS measurements. The estimated uncertainty of the contribution of fresh biomass burning is less than 30% and of the other primary sources less than 40%, when these sources contribute more than 20% to the total OA. The PMF uncertainty increases for smaller source contributions, reaching a factor of two or even three for sources which contribute ~~For contributions between 10 and 20% the corresponding uncertainties increase to 50%.~~

~~Finally, when these sources are small (~~less than 10% to~~of~~ the OA.~~) the corresponding error is a factor of two or even three.~~

One of the major questions in PMF analysis of AMS measurements concerns the sources of the two or more oxygenated OA (OOA) factors often reported in field studies. Our analysis suggests that these factors include secondary OA compounds from a variety of anthropogenic and biogenic sources and do not correspond to specific sources. Their characterization in the literature as low and high volatility factors is probably misleading, because they have overlapping volatility distributions. However, the average volatility of the one often characterized as low-volatility factor is indeed lower than that of the other (high volatility factor). Based on the analysis of the PMCAMx-SR predictions, the first oxygenated OA factor includes mainly highly-aged OA transported from outside Europe, but also highly aged secondary OA from precursors emitted in Europe. The second oxygenated OA factor contains fresher SOA from volatile, semi-volatile, and intermediate volatility anthropogenic and biogenic organic compounds. The exact contribution of these OA components to each OA factor depends on the site and the prevailing meteorology during the analysis period.

1. Introduction

Exposure to high levels of fine atmospheric particles results in increased mortality and morbidity (Pope et al., 2009). The same particles affect climate by scattering and absorbing solar radiation (Seinfeld and Pandis, 2006), and also influence the properties and lifetime of clouds (IPCC, 2014). Organic aerosol represents an important fraction (20 to 90%) of fine particulate matter (Kanakidou et al., 2005; Zhang et al., 2007) and is generated from biogenic and anthropogenic sources (de Gouw and Jimenez, 2009). It is usually characterized as primary (POA) when it is emitted directly in the particulate phase and secondary (SOA) when formed during the atmospheric oxidation of volatile, intermediate volatility, and semivolatile organic components.

The aerosol mass spectrometer (AMS) is a state-of-the-art instrument that can measure continuously the fine OA concentration providing at the same time unit or high resolution mass spectra of the OA. These spectra can be used in factor analysis to acquire information about OA sources, processes, and properties (Zhang et al., 2011). Several factor analysis techniques have been developed to estimate the contributions of sources and processes to the observed OA. These techniques include custom principal component analysis (Zhang et al., 2005), multiple component analysis (Zhang et al., 2007), positive matrix factorization (PMF) (Paatero and Tapper, 1994; Lanz et al., 2007) and the multilinear engine (ME-2) (Paatero, 1999; Lanz et al., 2008; Canonaco et al., 2013).

Zhang et al. (2005) separated the OA in Pittsburgh into an oxygenated OA factor (OOA) associated with secondary sources and a hydrocarbon-like OA factor (HOA) that represents POA related with urban sources and fossil fuel combustion. Lanz et al. (2007) identified additional important primary sources like biomass burning OA (bbOA). Measurements in Beijing showed that coal combustion (CCOA) is a major primary source in that area (Sun et al., 2013). Allan et al. (2010) identified cooking OA (COA) as a significant component of urban OA. However, Dall'Osto et al. (2015) argued that the interpretation of the COA factor may be problematic as it may include OA from other sources and not just cooking. Kostenidou et al. (2018) also argued that the bbOA factor determined in the South US by Xu et al. (2017) may include oxygenated OA from other sources. Yuan et al. (2012) suggested that PMF factors may correspond to different stages of photochemical processing, rather than to independent sources. Aiken et al. (2009) found that PMF can also yield factors that represent more than one source, especially in heavily polluted areas, due to their complex emission patterns. Brinkman et al. (2006) reported that when contributions from a pair of sources, such as diesel and gasoline exhaust, were highly correlated in synthetic datasets, a single factor corresponding to both sources was usually found. Despite these advances the accuracy of the PMF-determined primary organic sources remains an issue of debate.

OOA represents a significant fraction of OA at many locations (Zhang et al., 2007). Lanz et al. (2007) further separated OOA into more oxygenated OA (OOA-1) and less oxygenated OA (OOA-2) during summer in Zurich. Ulbrich et al. (2009) also reported an OOA-1 and an OOA-2 factor in Pittsburgh repeating the original analysis of Zhang et al. (2007). Typically, PMF of ambient AMS data identifies two types of OOA: a more oxidized OOA factor (OOA-1) which is thought to be more aged and almost non-volatile and a less oxidized factor (OOA-2) which is thought to be semivolatile (Jimenez et al., 2009; Ng et al. 2010). Huffman et al. (2009a) have showed that OOA-2 is usually more volatile than OOA-1 and includes less oxygenated secondary material (Jimenez et al., 2009). Jimenez et al. (2009) used the acronyms LV-OOA (low volatility) and SV-OOA (semivolatile) for OOA-1 and OOA-2, respectively. Paciga et al. (2016) using volatility measurements in Paris confirmed that SV-OOA is more volatile on average than LV-OOA, but argued that they both contain components with a wide range of overlapping volatilities. Kostenidou et al. (2015) proposed that the use of the SV-OOA and LV-OOA may be misleading and used the terms very oxygenated OA (V-OOA) and moderately oxygenated OA (M-OOA). Hildebrandt et al. (2010) based on measurements in Finokalia, Greece proposed that the two OOA factors represent the more and less oxidized states of secondary OA during the period of the analyzed field measurements. They suggested that in remote areas during photochemically active periods the two OOA factors are quite similar to each other as the OA is always at a very aged state. Other interpretations of the two OOA factors have also been proposed. For example, the less oxidized OOA (OOA-2) appeared to resemble biogenic SOA (bSOA) and the more oxidized OOA (OOA-1) appeared to be associated with transported OA from other areas in a study in Canada (Kiender-Schar et al., 2009; Sun et al., 2009). In most of the above studies OOA-1, LV-OOA, and MO-OOA have been used as names for the same factor. The same applies to OOA-2, SV-OOA, and LO-OOA.

Modeling efforts have so far focused on the comparisons of the factor analysis results of AMS measurements and the concentrations of modeled OA (Hodzic et al., 2010; Fountoukis et al., 2014; Tsimpidi et al., 2016). All these studies implicitly assume that each factor determined by PMF analysis of the AMS measurements corresponds to one group of sources.

In this work, we apply PMF analysis to the OA predictions of a chemical transport model in order to investigate whether PMF is able to separate the OA components from different sources or processes. Our main objective is to gain insights about the nature of the primary (POA, bbOA, etc.) and secondary (OOA-1, OOA-2, etc.) factors often determined in field studies and to quantify the corresponding uncertainties. Our analysis assumes that each OA component in the model is chemically different than the rest. This is not the case in reality as different OA components may have similar AMS spectra. As a result, our analysis represents to some extent a best case scenario.

However, the fact that the true sources and processes are known in this case makes this approach potentially useful.

2. Model Description

2.1 PMCAMx-SR

The model used in this study is the three-dimensional regional CTM PMCAMx-SR (Theodoritsi and Pandis, 2018)~~, a regional three-dimensional CTM~~. The major difference of PMCAMx-SR from its sister model, PMCAMx, is its ability to simulate separately the primary and secondary OA from different sources. Therefore, one can use different volatility distributions and aging schemes for organic compounds from different sources. PMCAMx-SR was applied to a 5400×5832 km^2 region covering Europe with 36×36 km grid resolution and 14 vertical layers extending up to 6 km. The model was set to perform simulations on a rotated polar stereographic map projection. The necessary inputs to the model include horizontal wind components, temperature, pressure, water vapor, vertical diffusivity, clouds, and rainfall. All meteorological inputs were created using the meteorological model WRF (Weather Research and Forecasting) (Skamarock et al., 2005).

The gas-phase chemical mechanism of PMCAMx-SR is based on an updated version of the SAPRC99 mechanism with 211 reactions of 56 gases and 18 radicals ~~consisting of~~including parameterizations, based on the 1D-Volatility Basis Set (VBS), of the gas-phase oxidation of semivolatile organic compounds (SVOCs) and~~,~~ intermediate volatility organic compounds (IVOCs) and volatile organic compounds (VOCs). The OA composition is described in PMCAMx-SR using a set of lumped species distributed across a VBS (Donahue et al., 2006) with volatility bins (surrogate species) that have saturation concentration C^* ranging from 0.01 to 10^6 μg m^{-3} separated by one order of magnitude at 298 K. Primary organic compounds are all treated as semivolatile, so their partitioning between the gas and particulate phases is simulated. The ~~considered to be semi-volatile~~simulated ~~with~~ C^* range of primary organic compounds ~~ing~~in the VBS ranges in this application from ~~from~~ 10^{-2} to 10^6 μg m^{-3} at 298 K (Shrivastava et al., 2008). Anthropogenic SOA (aSOA) and biogenic SOA (bSOA) are described separately using four volatility bins (1, 10, 100, 1000 μg m^{-3}). The secondary organic aerosol (SOA) formation and growth follows Murphy and Pandis (2009). The SOA module incorporates NO_x-dependent SOA yields (Lane et, al. 2008b) and contains anthropogenic aerosol yields based on the studies of Ng et al. (2006) and Hildebrandt et al. (2009). The volatility distribution proposed by Shrivastava et al. (2008) was used assuming that the mass of IVOC emissions is approximately equal to 1.5 times the primary organic aerosol emissions (Robinson et al., 2007; Tsimpidi et al., 2010). This POA volatility distribution is used in PMCAMx-SR for all sources with the exception of biomass burning. PMCAMx-SR simulates separately the fresh biomass burning organic aerosol (bbPOA) and its secondary oxidation products (bbSOA) using the volatility distribution of May et al. (2013) for the corresponding emissions.

Chemical aging in PMCAMx-SR is simulated assuming that the dominant pathway is gas-phase oxidation of the corresponding organic compounds by OH, assuming a rate constant equal to 1×10^{-11} cm^3 $molec^{-1}$ s^{-1} for anthropogenic SOA components and 4×10^{-11} $cm^3 molec^{-1}$ s^{-1} for the primary OA components and IVOCs (Murphy and Pandis, 2009). Each reaction leads to one order of magnitude reduction of the volatility of compound. The increase of the OA concentration due to the chemical aging of biogenic SOA (bSOA) is assumed to be negligible. The production of SOA by aqueous-phase chemistry is not simulated in this version of PMCAMx-SR.

The simulation period is May 2008, a warm summer-like month for most of Europe. This period was selected because PMCAMx has been evaluated against measurements from the EUCAARI campaign that took place during that month (Fountoukis et al., 2011). Fountoukis et al. (2014) in a subsequent study found encouraging agreement between predictions of PMCAMx and ME-2 analysis of AMS data for OA.

The boundary conditions used in this study are the same as in Fountoukis et al. (2011). The constant values used are based on measured average background concentrations in sites close to the boundaries of the domain. The boundary OA is assumed to be highly aged and to have low volatility ($C^*=0.01$ μg m^{-3}).

For the PMF analysis of the PMCAMx OA predictions, we created a matrix **X** in which each column consists of the hourly PMCAMx-SR predicted concentrations of POA, SOA-sv and SOA-iv, biomass burning POA, biomass burning SOA, anthropogenic SOA, biogenic SOA and long range transport (OA transported from outside the model domain). The material in each bin with $C^* \leq 10^2$ μg m^{-3} was included in the PMF analysis as an independent OA component. The OA in volatility bins with higher saturation concentrations was excluded, because its particulate phase concentrations are negligibly small or zero. PM$_1$ was used to our analysis for consistency with the AMS measurements. However, the difference in predicted OA in the PM$_{2.5}$ and PM$_1$ range is small in PMCAMx-SR so our conclusions are also valid for PM$_{2.5}$.

Table S1 provides a complete list of the 27 OA components used in our PMF analysis. We implicitly assume that each OA component is "chemically different" from the others. As we provide PMF with the concentrations of 27 different predicted OA surrogate components, we implicitly assume that the corresponding measurement technique or techniques can separate and quantify these components. For the AMS, this may not be the case as two OA components (e.g., processed bbOA and aged SOA) may have quite similar AMS spectra.

2.2 Particulate Source Apportionment Technology

PSAT is a computationally-efficient source apportionment algorithm for studying PM source apportionment contributions (Wagstrom et al., 2008) extended by Skyllakou et al. (2014) to include OA simulated with the VBS. Skyllakou et al. (2018) used (PSAT) together with the volatility basis set framework (Donahue et al., 2006) to estimate the age of the OA components in Europe during the same period as in this study. In this application, the PSAT algorithm works in parallel with the CTM and provides the "fresh" secondary components (first generation), the products of two generations of reactions, etc. These results of Skyllakou et al. (2018) are used here.

In order to apply PMF to the results of PSAT we generated a matrix **X** which includes the hourly concentration of OA components categorized as "fresh", long range transport OA, fresh biogenic SOA, fresh anthropogenic SOA, aged (second and later)

SOA-sv and SOA-iv with each saturation concentration (C^*) ranging from 0.01 to 100. Table S2 shows the 19 OA components used in this PSAT-based PMF analysis.

2.3 Positive Matrix Factorization (PMF)

PMF (Paatero and Taaper, 1994) is a bilinear model that has been used for the quantification of the sources of airborne particulate matter measurement. PMF decomposes the 'observation' matrix X into two matrices **G** and **F**:

$$x_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij} \tag{1}$$

where x_{ij} are the measurements used as the PMF inputs, g_{ik} are the contributions of sources, f_{kj} are the factor profiles and e_{ij} the residuals of the analysis. The subscript i corresponds to time, j to the compounds and p is the number of factors. Factor profiles and time series are derived by the PMF model minimizing the objective function Q:

$$Q = \sum_{i=1}^{m} \sum_{j=1}^{n} \left(\frac{e_{ij}}{u_{ij}} \right)^2 \tag{2}$$

where u_{ij} are the data uncertainties with the constraint **G** and **F** matrices to be positive. In this study we used 5%, 10% and 20% uncertainty for each data point of matrix **U** and we did not observe significant differences in the results. For this reason, a 10% uncertainty is assumed for each data point.

In this work, we first created the matrices **X** and **U** in proper format consistent with EPA PMF v5.0. Then, we ran PMF assuming 2, 3, 4 factors and so on. For the selection of the number of factors that best describes our data we used a series of metrics. We first examined the change of Q/Q_{exp} for each solution. Q is the sum of the squares of the scaled residuals and Q_{exp} represents the ideal value if the residuals were the same as the uncertainty assumed for each data point. We then examined the residuals of the model as a function of the number of factors. We also estimated the correlation coefficients of the time series of the factors determined by PMF. If a pair of factors was strongly correlated, we reduced the number of factors. We also checked the composition of each factor. If there is a pair of factors with similar composition, this solution is rejected. For the chosen solution, we also investigated the change of factor profile with positive and negative values of *fpeak*. If the factor profiles are insensitive to the *fpeak* choice, we proceeded with *fpeak* equal to zero.

Factor analysis methods are in general based on the temporal correlation among the concentrations of different pollutants. However, in their effort to limit the dimensionality of the chemical (or AMS *m*/*z*) space, these approaches distribute the pollutants into factors in ways that are by no means transparent. Our goal in this work is to shed a little more light on what PMF does when it is applied to the AMS organic aerosol data. The PMF analysis in this work was performed using the PMCAMx-SR predictions for each site separately. The sites were selected to cover a wide range of conditions and source contributions. For example, we chose Majkow Duzy (Poland) because it has the highest predicted contribution of POA to OA. St. Petersburg, Catania and Majden are three locations in different environments with bbOA during the simulation period. Melpitz, Cabauw and Finokalia were chosen because there are AMS measurements available for the simulation period and they also cover quite different environments. Other sites were chosen because they had different predicted bbOA/OA levels.

2.4 The Multilinear Engine (ME-2)

In selected cases, we also used the multilinear engine (ME-2) algorithm (Paatero, 1999) implemented within the toolkit Sofi (Source Finder) developed by Canonaco et al. (2013). We used ME-2 in areas in which an HOA factor was not found by PMF. For the selection of the number of factors, we followed similar steps as with PMF. The main difference with PMF analysis is that we introduced the vector F_j (factor profile) which includes only the contribution of POA components with the rest of the OA components having zero contribution to this factor. The ME-2 algorithm a value determines the extent to which the output factor profile can vary from the factor profile which we provide (Canonaco et al., 2013). We used a=0.1 for our analysis. We also examined different values of a ranging from 0 to 0.3, but our results were not sensitive to that choice.

3. Results and discussion

3.1 PMCAMx-SR R~~r~~esults

The predicted average OA at the ground level was 1.8 μg m^{-3} during the simulation period with average concentrations as high as 4 μg m^{-3} in central and north-eastern Europe (Fig. S1a). The average concentration of POA was 1.4 μg m^{-3} with the highest levels predicted in northern Europe (Fig. S1b). SOA levels were higher in central Europe (Fig. S1c). Details about these predictions can be found in Fountoukis et al. (2011; 2014) and Theodoritsi and Pandis (2018).

3.2 Application of PMF to PMCAMx-SR OA

We first analyse the PMCAMx-SR OA predictions in Melpitz (Germany) because there were AMS measurements and corresponding PMF results available in this site during the same period. The average PMCAMx-SR predicted OA in that site was 4.2 μg m^{-3}, while the observed OA was 5.3 μg m^{-3}. PMCAMx-SR predicted that long-range transported OA contributed 24%, biogenic SOA 23%, SOA from SVOCs and IVOCs 20%, anthropogenic SOA 18%, biomass burning SOA 10%, POA 3% and biomass burning POA 2% to the total OA. The AMS PMF analysis did not identify a POA or a fresh biomass burning OA factor for the corresponding period (Poulain et al., 2014), a result consistent with the low predicted contributions of these two sources.

The 2-factor PMF solution explained the PMCAMx-SR OA predictions. A 2-factor solution had also been found by Poulain et al. (2014) during their PMF analysis of the field measurements in the same period. The first PMCAMx-SR factor includes a variety of secondary OA components: biomass burning SOA (10%), anthropogenic SOA (20%), biogenic SOA (45%) and SOA-sv and SOA-iv (20%) (Fig. 1). It contains mostly SOA (around 95%) and therefore will be called “SOA factor” (Fig. 1). The second factor contains mostly (50%) OA from long range transport and therefore will be called ‘LRT factor’. The remaining 50% of the LRT-factor is mainly anthropogenic SOA (14%), SOA-sv and SOA-iv (24%) and biomass burning SOA (10%). The SOA-factor contributed 53% to the predicted OA while the LRT-factor 47%. The concentrations of both factors were quite variable (Fig. 2), but the SOA factor fluctuated more than the LRT factor.

During the same period two factors were identified analyzing the AMS measurements in Melpitz: low-volatility oxygenated OA (LV-OOA) and a semi-volatile oxygenated OA (SV-OOA) factor (Poulain et al., 2014). The average diurnal profile of the PMCAMx-SR SOA factor follows the same pattern as SV-OOA (Fig. 3a) with higher values during the night. The PMCAMx-SR LRT factor is less than the AMS LV-OOA factor during the day. These differences can be due to model errors or can be actual differences in the PMF analysis of the two data sets.

The above results are quite encouraging. This analysis of the two data sets suggests that the PMCAMx-SR PMF analysis provides results that are similar with the corresponding analysis of the AMS measurements. Both approaches result in two oxygenated OA factors. Even more the AMS LV-OOA factor appears to correspond to the LRT factor of PMCAMx-SR, and the AMS SV-OOA factor to the PMCAMx-SR SOA factor. We will return to the Melpitz dataset in a subsequent section focusing on OOA. In the next two sections we focus on the major primary OA factors.

3.2.1 Biomass burning organic aerosol

In this section, we examine whether the PMCAMx-SR factor which represents biomass burning (bbOA) sources consists of only bbOA components. In St. Petersburg (Russia) PMCAMx-SR predicted hourly bbOA levels exceeded 200 μg m^{-3} due to the nearby fires affecting the site on May 4-5 (Fig. S2~~4~~a). During the full month in this site, the average contribution of fresh biomass burning OA to the total OA was approximately 65%. During the fire period (4-5 of May) the bbOA contribution was 96%. The 4-factor PMF solution seems to best represent the PMCAMx-SR OA predictions in St. Petersburg. PMF determined a factor which consists of 96% biomass burning POA and low contributions from biogenic SOA and biomass burning SOA components (Fig. 4~~5~~). This factor will be called “bbPOA factor”. In this case, the bbPOA factor includes little else. Comparing the time series of the bbPOA factor and the bbPOA predicted by PMCAMx-SR we estimated a fractional error of 5% and a fractional bias of -3% (Table S3).

In Catania (Italy) the hourly bbPOA concentration exceeded 35 μg m^{-3} during May 15-17 due to nearby fires (Fig. S2~~4~~b). During the fire period, the contribution of bbPOA to OA reached 94%. During the full month, the average bbPOA contribution to the total OA was 40%. A 3-factor PMF solution was selected in this case. PMF determined a factor with 93% biomass burning POA and the remaining 7% was biomass burning SOA (4%), biogenic SOA (2%) and anthropogenic SOA (1%) in (Fig. 4~~5~~). The corresponding normalized error when the time series of the bbOA factor was compared to the PMCAMx-SR bbOA predictions was 11% in this case.

In Majden (FYROM) fires contributed up to 15 μg m^{-3} of bbPOA on May 25-26 and bbPOA was 75% of the OA during the fire period (Fig. S2~~4~~c). The average bbPOA contribution to OA was 14% during the simulation period. The 3-factor PMF solution best fit our data. PMF identified a factor consisting of 81% bbPOA, 11% biogenic SOA, 4% long range transport OA, 2% biomass burning SOA and 2% anthropogenic SOA (Fig. 4~~5~~). The corresponding normalized error comparing this factor against the actual bbPOA was 24% due to the mixing of the fresh bbPOA with secondary OA from other sources by the PMF.

In Cabauw bbPOA contributed 8% to OA according to PMCAMx-SR with an average concentration of 0.4 μg m^{-3}. There were no major fires nearby and the predicted hourly bbPOA concentration was always less than 3 μg m^{-3}. The bbPOA in this case was included by the PMCAMx-SR PMF in a “bbPOA/SOA” factor. This factor is called bbPOA/SOA because it consisted of bbPOA and SOA components. The PMF analysis did not give a bbPOA factor even when 5 factors were used. The same lack of a bbPOA factor was found in the analysis of the PMCAMx-SR OA in Melpitz and Finokalia. The maximum predicted hourly concentration of bbPOA in Melpitz was 0.5 μg m^{-3} and in Finokalia 0.1 μg m^{-3}. The bbPOA in these areas was less than 2% of the OA.

In areas affected by major fires (St. Petersburg, Catania and Majden) the maximum predicted hourly concentration of bbSOA was 12, 6.5 and 5.7 μg m^{-3}, respectively. In all areas examined in this study bbSOA was included mainly in one of the OOA factors which will be discussed in detail in the next section. This is due to the fact that the temporal evolution of bbSOA is closer to that of the other SOA components. Therefore, the contribution of biomass burning determined by PMF represents a lower estimate of the impact of fires to OA in a receptor since it includes only a small fraction of the bbSOA.

3.2.2~~3~~ Primary organic aerosol

The ability of PMF to identify the fresh POA from sources other than biomass burning is explored in this section. POA according to PMCAMx-SR contributed 10% to OA during May in St. Petersburg. The 4-factor PMF solution included a factor which consisted of 67% POA (Fig. 5~~6~~). The remaining was SOA-sv and SOA-iv (9%), biogenic SOA (6%), anthropogenic SOA (5%), biomass burning POA (8%) and biomass burning SOA (5%). We call this “POA factor”, but it clearly includes other OA components. For the purposes of our analysis, we consider that PMF identifies a POA factor if there is a factor containing more than 60% POA. The POA factor and PMCAMx-SR POA concentrations were well correlated to each other (R^2=0.99, Fig. S3~~2~~). The average concentration of the POA factor was 1.1 μg m^{-3} and of the actual POA 0.9 μg m^{-3}. The normalized error of the POA factor compared to the PMCAMx-SR POA was 34% (Table S4).

The highest contribution of POA to total OA was predicted in Majkow Duzy in central Poland and it was 50%. In this location, the POA contributed 90% to the corresponding POA factor (Fig. 5~~6~~). The remaining was biogenic SOA (3%), long range transport OA (4%), anthropogenic SOA (1%), biogenic SOA (1%) and biomass burning SOA (1%). The average concentration of the POA factor was 3.2 μg m^{-3}, while the PMCAMx-SR actual POA was 3.4 μg m^{-3}. The normalized error of the POA factor 10% in this case (Table S4).

In rural and remote sites (Cabauw, Melpitz and Finokalia) POA contributed around 3% to the total OA according to PMCAMx-SR. In Cabauw the 3-factor solution included factors which contained 6%, 11% and 10% POA, respectively. In the 4-factor solution POA contributed 12%, 10%, 5% and 0% to the factors. In these areas, PMF did not separate the POA from the rest of the OA components.

3.3~~4~~ PMF Source Apportionment E~~e~~rror for P~~p~~rimary OA C~~c~~omponents

The above analysis of the bbOA and POA factors suggests that the corresponding PMF error does depend on the magnitude of the contribution of the corresponding source to the total OA levels. Higher relative errors are estimated when a source contributes less to the total OA. To better quantify the corresponding dependence of the error on the magnitude of the source we used the PMF solutions in a number of locations and we also artificially scaled up and down the predicted bbOA and POA in certain locations (St. Petersburg, Maiden, Catania, Cabauw, and Majkow Duzy) and repeated the PMF analysis. The results are summarized in Fig. 6~~7~~.

The normalized mean error of the bbPOA estimated by the PMF is less than 30% when the bbPOA contributes more than 20% to the total OA in the area. The error is reduced to less than 20% for contributions higher than 30%. On the other hand, when the bbPOA represents 10-20% of the total OA the PMF error can be up to 50%. When biomass burning contributes less than 10% the error increases to a factor of 2-3. Please note that in these cases, the absolute error is still reasonable and the PMF correctly predicts that bbOA is a relatively small component of OA.

The uncertainty in POA from other sources appears to be a little higher than that of bbPOA probably because PMF mixes it with other sources that have similar temporal profiles. When the POA represents more than 20% of the OA, the PMF error is less than 40%. The errors can be up to a factor of 2, when the POA is less than 20% of the OA.

3.4~~5~~ Oxygenated Organic Aerosol

In this section we try to determine the characteristics that differentiate the two OOA factors that are often present in ambient AMS data analysis. One hypothesis is that the two OOA factors contain different OA components (e.g. anthropogenic versus biogenic). A second hypothesis is that one represents the semivolatile and the other the low-volatility OA components. The third hypothesis is that these two factors have different degrees of aging (one is relatively fresh SOA and other SOA that has undergone multiple generations of oxidation).

The two PMCAMx-SR OOA factors in all areas consist mainly of multiple SOA components. The first OOA factor determined by PMF analysis of PMCAMx-SR OA predictions contains mainly OA from long range transport. This factor was determined in all areas examined.

In St. Petersburg long range transport (LRT) OA was 11% of the OA according to PMCAMx-SR. The 4-factor solution included a factor which contained 55% LRT-OA and is described here as the "LRT factor" (Fig. 7~~8~~). In Majden the contribution of LRT-OA to total OA was 25%. In this area PMF determined a LRT factor with 68% long range transported OA. In Catania LRT OA contributed 29% to OA and the LRT factor consists of 70% LRT-OA. In Cabauw and Melpitz the contribution of long range transport OA was 21% and 24% and the corresponding LRT factors consist of 58% and 48% LRT-OA, respectively. During May, the highest contribution of LRT-OA to total OA was determined in Finokalia and it was around 40%. In this site, the LRT-OA contributed 87% to the LRT factor (Fig. 7~~8~~). Thus, the contribution of highly aged OA transported from outside the domain to the LRT factor ranges from approximately 50% to 90% for the areas examined.

The second OOA factor determined in all areas contains SOA-sv and SOA-iv, anthropogenic SOA, biomass burning SOA and biogenic SOA (Fig. 8~~9~~). We call this "SOA factor" because it mostly includes SOA produced inside the modeling domain. In Catania, PMF combines bbSOA (20% contribution to SOA factor), aSOA (20%) and SOA-sv and SOA-iv (30%) in the SOA factor because the time series of these OA components follow a similar pattern during the simulation period (Fig. S4~~3~~). This is also the case in the other areas (Majden, Melpitz and Finokalia, Figs. S5~~4~~-S7~~6~~) examined. The contribution of each SOA component to the SOA factor depends on the examined area. Therefore, the SOA factor consists of a mixture of contributions from various anthropogenic and biogenic sources.

While the two OOA factors both include a mixture of all SOA components (Figures 8 and 9) the LRT factor is dominated by the highly aged OA transported to Europe from outside the domain, while the SOA factor includes mainly SOA produced over Europe. Therefore, the hypothesis that PMF separates the SOA components based on their sources (e.g. biogenic versus anthropogenic) is not supported by our results.

3.4~~5~~.1 Volatility of OOA factors

We analyzed the volatility distribution of the two PMCAMx-SR OOA factors predicted by PMCAMx-SR in order to examine whether these factors include OA components with different volatility. In Melpitz the volatility distribution of the SOA factor peaks at effective saturation concentration equal to 1 μg m^{-3} (Fig. 9~~10~~a). 90% of the OA in this factor has effective saturation concentration (*C**) higher or equal to 1 μg m^{-3}. On the other hand, the LRT factor is dominated by components with *C** equal to 0.01 and 0.1 μg m^{-3}, contributing 80% to the factor. In Finokalia the highest mass fraction of the LRT factor has effective saturation concentration equal to 0.01 μg m^{-3} (Fig. 9~~10~~c). The LRT factor in this case contains almost exclusively low volatility OA. The SOA factor includes both low volatility and semivolatile components. In St. Petersburg, Catania and Majden the results for the volatility distribution of LRT and SOA factor were between those in St. Petersburg and in Finokalia (Fig. S8~~7~~).

These results suggest that both factors have components covering a wide range of volatilities and their volatility distributions overlap. However, the LRT factor has on average lower volatility than the SOA factor. These suggest that the PMF does not separate these factors exclusively based on the volatility of the corresponding components. For example, in Melpitz both factors include a lot of OA with *C** equal to 1 μg m^{-3}.

The use of the volatility-based terminology (low volatility and semivolatile OOA) suggests that there is a volatility threshold and OA components that are more volatile than this are grouped by PMF in one factor (e.g., SV-OOA) and the less volatile compounds in the second (LV-OOA). Our results both from this theoretical analysis but also from direct volatility measurements of AMS factors (Paciga et al., 2016; Louvaris et al., 2017) show that this is not the case. The so-called semivolatile factor may include very low volatility OA and vice versa the so-called low-volatility factor may include semivolatile material.

3.4~~5~~.2 The degree of aging of OOA factors

We applied PMF analysis to PSAT results, separating all the SOA components into two subcategories: first generation and later generation products (second, third, etc.), to investigate whether the degree of chemical processing differentiates the two OOA factors.

In Melpitz the first PMCAMx/PSAT factor consists of 63% first generation OA and 37% later generation OA and is called the “less aged factor” (Fig. 10~~1~~). The second factor includes 97% later generation OA and can be described as the “more aged factor”.

In the more remote site of Finokalia, we determined two factors which both contain aged OA. We characterize the first factor as “extremely aged” because highly aged long range transport OA dominated this factor (98%) (Fig. 10~~1~~). The second factor is characterized as “very aged” containing 32% later generation aSOA, 54% later generation SOA from semi-volatile and intermediate volatility organic compounds and only 14% first generation SOA. These results are consistent with the analysis of Hildebrandt et al. (2010) who argued that the OA behaviour in Finokalia is quite different that in continental European sites and that the two OOA factors are quite similar to each other. This is also predicted by PMCAMx-SR suggesting that the model is consistent with that interpretation of the measurements.

One of the limitations of this application of PMCAMx-SR is that we assumed low volatility constant OA boundary conditions. In general boundary conditions of regional chemical transport models are obtained from the output of similar global models or from some averages of measurements and can be a lot more variable (both in concentration but also in composition and volatility). Obviously, the absolute OA concentrations especially near the boundaries of the domain can be dominated by these boundary conditions. To avoid such issues, we have used in this analysis sites that are far from the boundaries. Overall, our conclusions are quite robust to the choice of the OA boundary condition values.

Our analysis suggests that the evolution of the terms used to describe the often observed two OOA factors reflects our understanding (or lack there-of) of the nature of these factors and not so much site to site variability. The use of OOA1 and OOA2 reflected the complete lack of understanding. Then the use of Less and More Volatile OOA showed the beginning of some understanding, but it has probably led to some confusion and a few misconceptions. The next step (use of Less and More Oxidized OA) is probably more accurate. Our work here supports the hypothesis that these factors correspond to Less and More Aged OOA present in each site.

3.4~~5~~.3 Comparison of OOA factors of PMF and ME-2 analysis

In this section, we compare the two OOA factors determined by PMF and ME-2 analysis in order to estimate the change of these factors when ME-2 analysis is used. In ME-2 we used the “correct” POA factor (forced the model to assume 100% contribution of POA to the POA factor). Moving from PMF to ME-2, the changes of the composition of the SOA and LRT factor were minor in all examined areas. Figures S9~~8~~ and S10~~9~~ illustrate the two OOA factors in Melpitz and in Finokalia when PMF and ME-2 are used. Thus, the above conclusions for the two OOA factors do not change when ME-2 is used. The gain of the use of ME-2 analysis is that a better separation of primary sources is obtained if of course the correct POA fingerprint is used.

3.5 Sensitivity Analysis

To better quantify the role of the volatility of the OA components on the results of the PMF analysis we repeated the PMF application on the PMCAMx-SR predictions using this time as inputs only the volatility distributions of the predicted total OA. In this case the PMF inputs were the total concentrations of OA in the five C^* volatility bins ranging from 10^{-2} to 10^{2} μg m^{-3}. We first assumed two factors. The resulting PMF factors included material from all volatility bins. For example, for St. Petersburg, the first factor contained 65% semivolatile OA and the second 70% with the rest being low volatility OA. So PMF did not separate the OA into semi-volatile and low volatility material. In the next step we assumed three factors but still the factors included surrogate compounds with a mixture of volatilities. These results suggest once more that the OA volatility plays a secondary role in the process in which PMF separates the OA components into factors.

In a second test, we performed PMF analysis on a dataset consisting of the PMCAMx-SR hourly predictions for six of the sites (St. Petersburg, Catania, Majden, Melpitz, Finokalia and Cabauw) used in the analysis in the previous sections. Something like this is rarely done with field data because it is assumed that the composition of the primary and secondary factors may be different in different area. Thus, the merging of the datasets may introduce additional uncertainties in the PMF analysis. In this case, the composition of all sources in all areas is assumed to be the same in PMCAMx-SR, so one can examine the behavior of PMF in this ideal situation. PMF could reproduce the overall dataset using four factors: a primary OA factor, a biomass burning OA factor and two secondary OA factors.

For the primary OA factors, applying PMF to the complete dataset resulted in factor compositions that had an intermediate composition compared to the factors from the site-by-site analysis. For example, the POA factor in the common analysis contained 81% fresh POA, a value close to the middle of the 67% for St. Petersburg and the 89% for Majkow Duzy (Fig. S11). The predicted concentrations of the POA factor in the site-by-site and common PMF were quite similar with differences less than 10% in the average predicted concentrations (Fig. S12). The same behavior was observed for primary bbOA, with the common analysis giving intermediate results but closer to the best than the average. The corresponding PMF bbOA factor contained 93% bbOA in this case (Fig. S13), a little less than the 96% in the independent analysis of the St. Petersburg predictions, but a lot more than the 81% in Majden. The bbOA factor time series for the site-by-site were once more quite similar to each other (Fig. S14) with differences in the average concentrations of less than 15%.

The situation was quite different for the OOA factors. The results of the common analysis were quite different from those of the site-by-site analysis in most but not all sites. For example, the common SOA factor contained 27% biogenic SOA, while the corresponding factors for the site-by-site analysis contained from approximately 5% to 42% bSOA (Fig. S15). It is interesting though, that the common SOA factor did not include any aged from long range transport. The resulting concentrations of the predicted SOA factor for the common analysis could be quite different from those of the site-by-site analysis. For example, in St. Petersburg the concentration of the SOA factor was 1.1 μg m^{-3} for the site-by-site analysis and 0.7 μg m^{-3} for the common analysis (Fig. S16). On the other hand, for Catania the results of the approaches were quite similar with average concentrations of 1.5 μg m^{-3} for the site-by-site and 1.3 μg m^{-3} for the common analysis (Fig. S17). The common LRT factor contained 73% OA from long-range transport a value closer to the upper limit (79% for Finokalia) than to the lower (47% for Melpitz) for the site-by-site analysis (Fig. S18). The average concentration of the LRT factor in Melpitz was 1.9 μg m^{-3} for the individual and 1.3 μg m^{-3} for the common analysis (Fig. S19). These results indicate that the composition of the OOA factors and the resulting concentrations are quite sensitive to the range of data included in the analysis.

4. Conclusions

We analyzed for the first time, to the best of our knowledge, the organic aerosol composition predictions of a chemical transport model (PMCAMx-SR) using positive matrix factorization in an effort to better understand the results of PMF analysis of ambient organic aerosol AMS measurements. The high-level results of our analysis are quite consistent with those of the corresponding field studies; we find similar number and characteristics of factors for a number of sites in Europe. This consistency indicates that the analysis of the model results can be used as a first order interpretation of the various factors often reported in field data PMF analysis. These factors include the hydrocarbon like OA and biomass burning OA and two oxygenated organic OA factors. Cooking OA was not included as a source in the emissions inventory used, so it cannot be studied at this stage.

The primary OA factor (which corresponds to the hydrocarbon-like OA in AMS analysis) of the PMCAMx-SR predictions usually contains not only primary OA compounds but also secondary components or biomass burning OA. These additional components represent on average one third of the factor mass. The average error of using HOA instead of POA is around 25% in the cases examined and increases when the POA contribution to OA decreases. PMF identifies a POA factor in the PMCAMx-SR predictions when this group of sources contributes more than 10% to the OA and is one of the top three sources.

PMF determines a biomass burning OA factor in all areas influenced by major nearby fires. In these cases of major fire influence, the biomass burning primary OA factor consists of around 90% biomass burning primary OA. The error in the bbPOA factor is less than 30%, when biomass burning contributes more than 20% to the average OA. The biomass burning secondary OA is grouped always with secondary OA components and only a small fraction of it is included in the biomass burning factor. Therefore, the bbOA factor provides a lower limit of the impact of fires on the OA of an area.

Our analysis suggests that PMF has difficulties identifying sources that contribute approximately 10% or less to the total OA during the period of the analysis. The use of ME-2 constraining the primary OA factor (which contains 100% contribution from primary OA) provides a better separation of primary and secondary sources reducing the contribution of POA to the two oxygenated OA factors. However, this assumes perfect knowledge of the "fingerprint" of the POA factor.

The two oxygenated OA factors both contain a series of SOA components from both anthropogenic and biogenic sources. The first oxygenated OA factor includes mainly highly aged OA transported from outside Europe, but also highly aged secondary OA from sources in Europe that has undergone multiple generations of oxidation. The second oxygenated OA factor contains SOA from volatile, semi-volatile, and intermediate volatility anthropogenic and biogenic organic compounds. The exact contribution of these OA components to each OA factor depends on the site. In rural continental areas (like Melpitz) the first oxygenated OA factor includes highly aged secondary OA and the second mostly "fresh" first-generation secondary organic compounds. On the other hand, in remote sites such as in Finokalia in Crete, both oxygenated OA factors include organic components that have undergone two or more generations of aging. This suggests that the PMF determines the two extremes of the chemical processing of the OA present in the site during the measurements and reports them as the corresponding OOA factors.

The two oxygenated OA factors have most of the time overlapping volatility distributions and therefore their characterization as low and high volatility that has been used in the literature ~~is probably~~may be misleading in at least some cases. This is consistent with the measurements of Paciga et al. (2016) in Paris and Louvaris et al. (2017) in Athens. However, the more aged factor has lower average volatility than the fresh secondary OA factor.

Our results suggest that the comparison of CTM predictions of POA and fresh biomass burning OA to the corresponding AMS results is meaningful if these are major sources for the specific locations. The PMF uncertainties estimated here should also be taken into account. The comparison of the less and more volatile OA predicted by CTMs to the corresponding OOA factors is probably not a good idea. Summation of the two OOA factors into just OOA appears to be quite safe, based on our results here. On the other hand, if a CTM can keep track of the age of OA the comparison of more and less aged predicted OA to the two OOA factors could be potentially useful.

Acknowledgements

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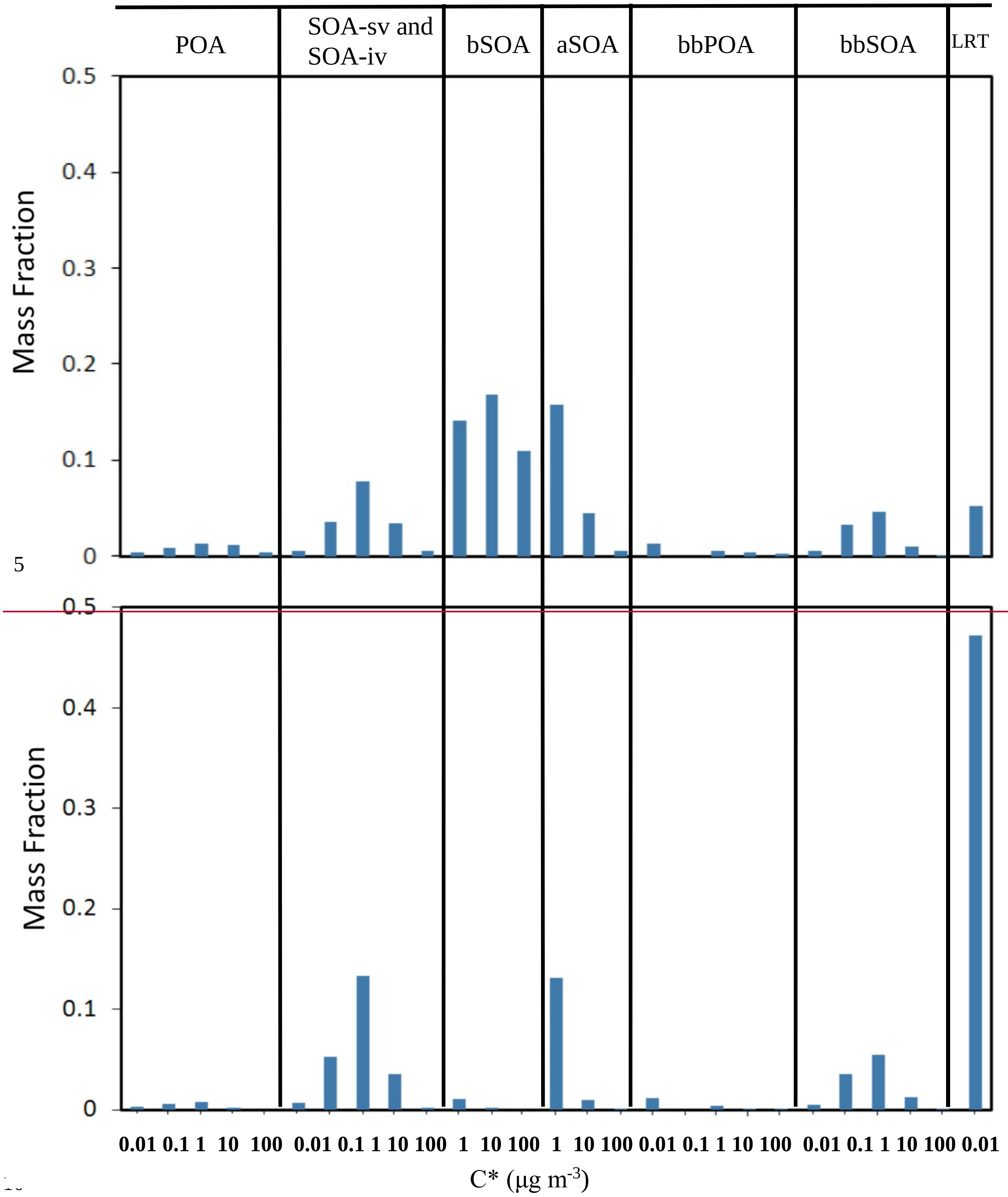
POA
SOA-sv and SOA-iv
bSOA
aSOA
bbPOA
bbSOA
LRT
Mass Fraction
0.5
0.4
0.3
0.2
0.1
0
Mass Fraction
0.5
0.4
0.3
0.2
0.1
0
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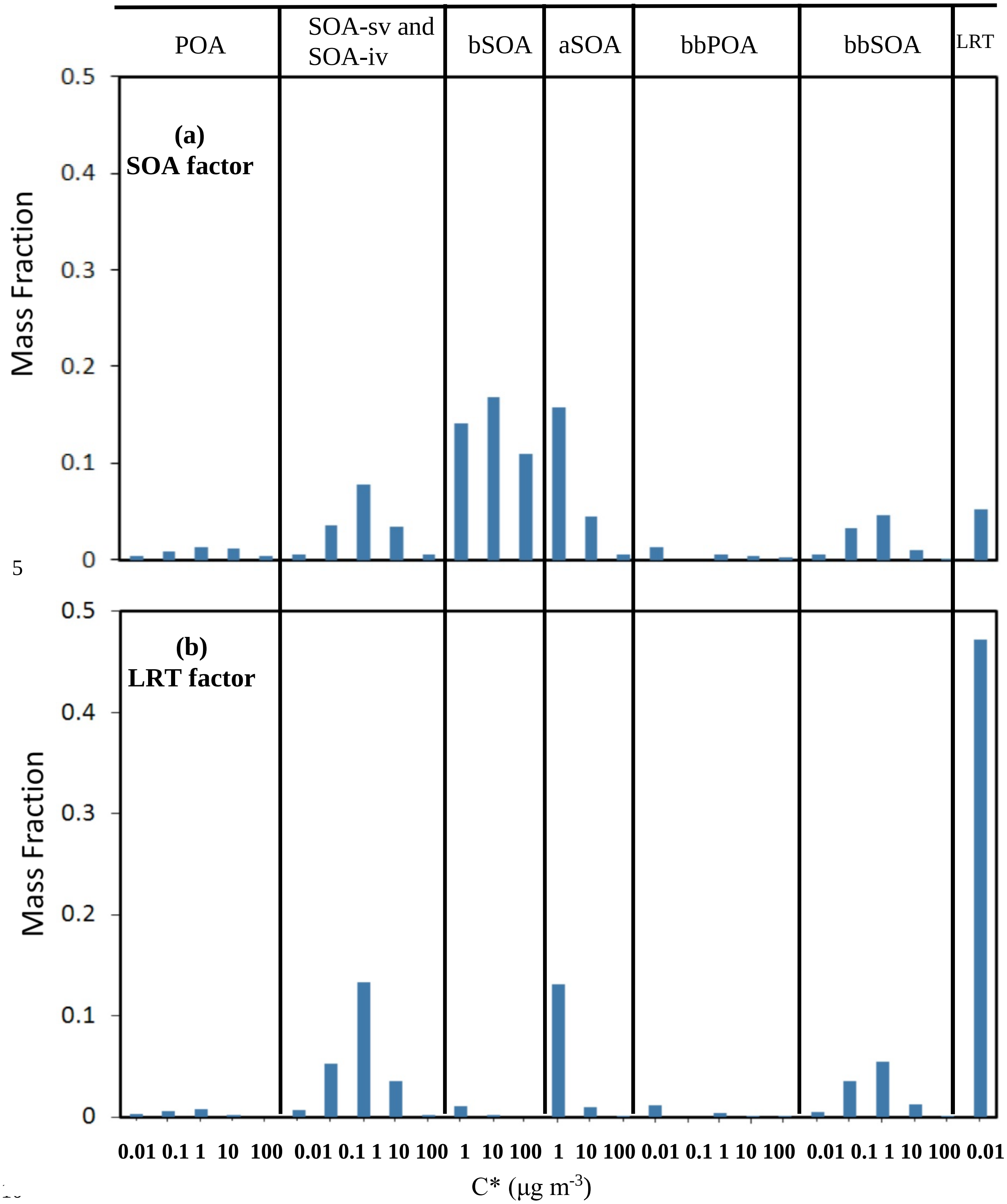


Figure 1. Factor profiles resulting from the PMF analysis of the PMCAMx-SR OA predictions in Melpitz: (a) SOA factor and (b) LRT factor.

~~**Figure 1.** SOA and LRT factor profiles resulting from the PMF analysis of the PMCAMx-SR OA predictions in Melpitz.~~

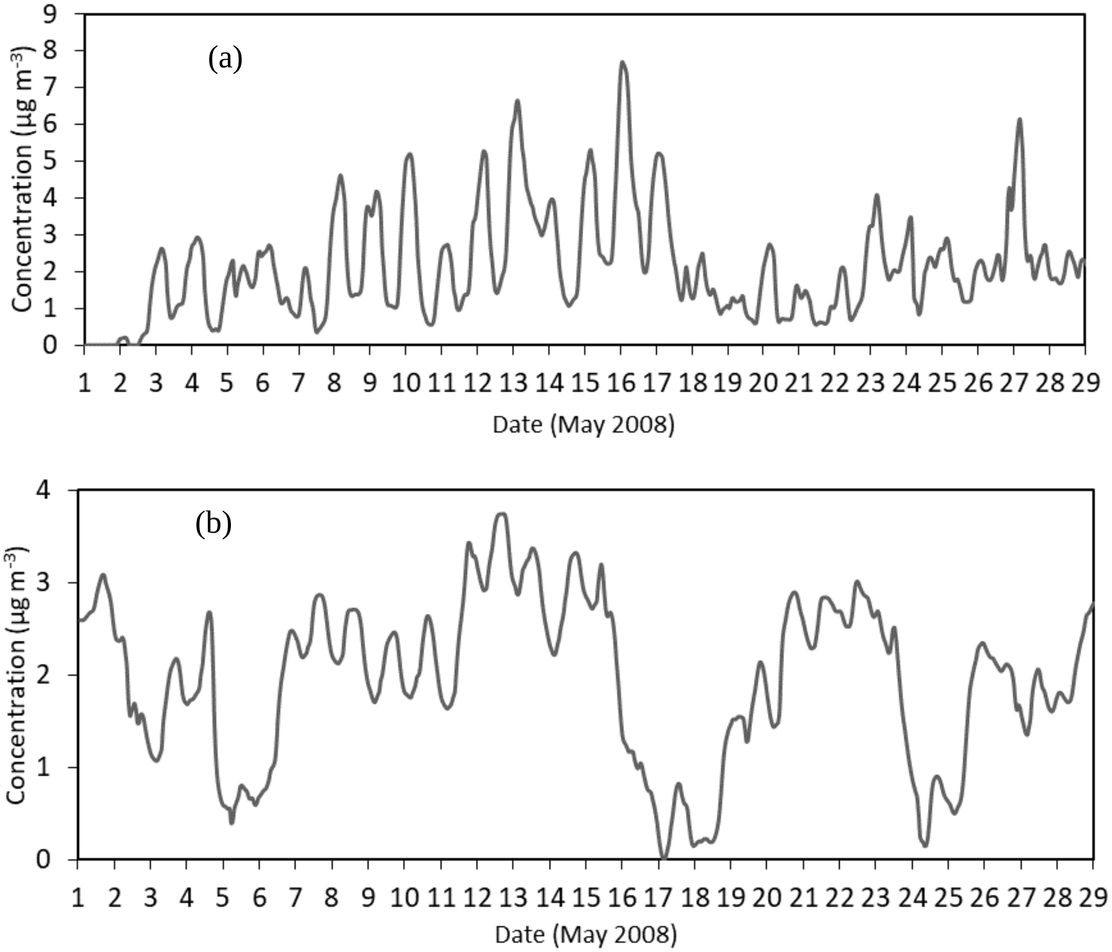


Figure 2. PMCAMx-SR factor time series of the: (a) SOA and (b) LRT factors in Melpitz during May 2008.

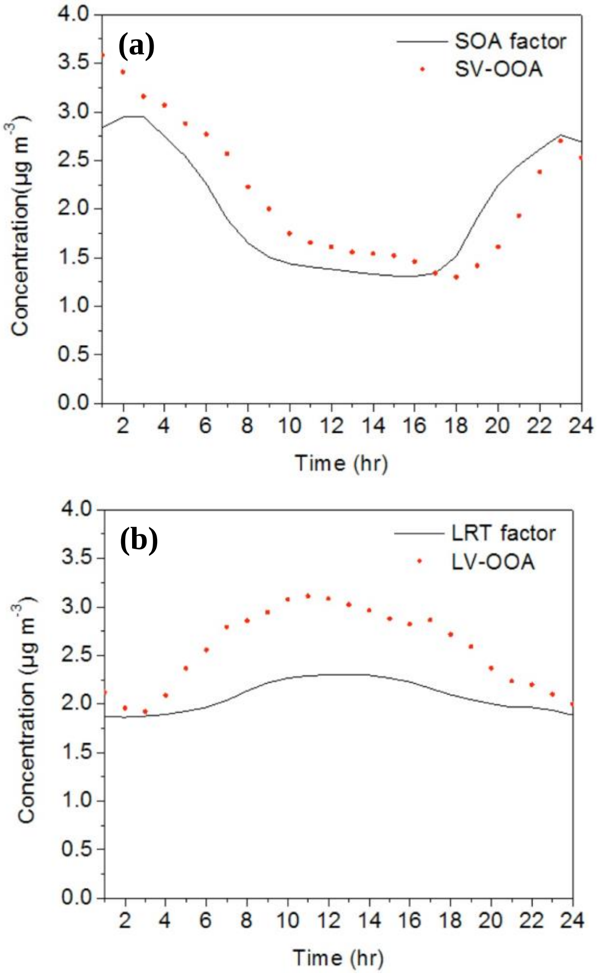
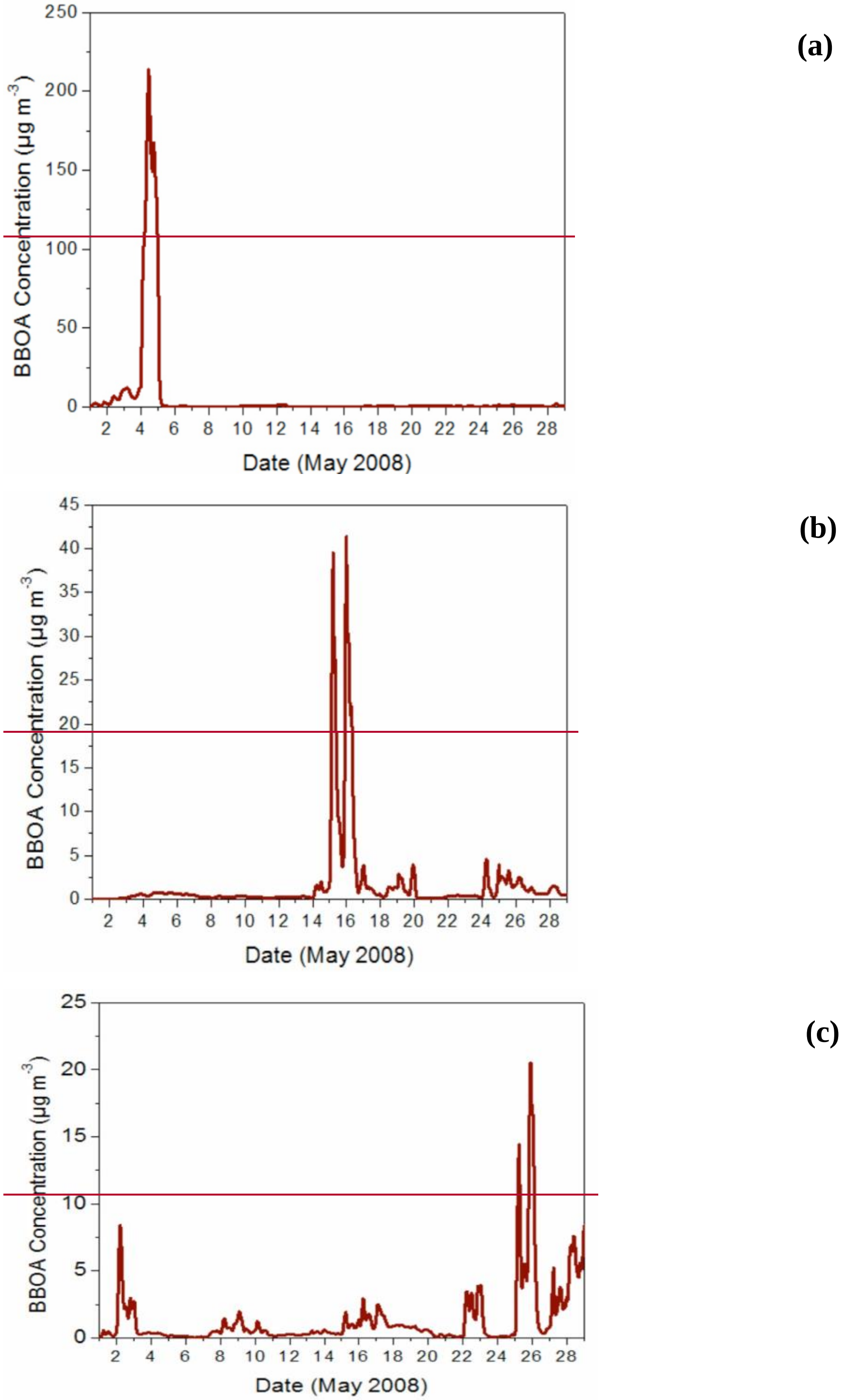


Figure 3. Comparison of average diurnal profiles of factors of PMF analysis of PMCAMx-SR results and PMF analysis of AMS measurements in Melpitz: (a) SOA factor and SV-OOA and (b) LRT factor and LV-OOA.



~~**Figure 4.** Time series of predicted biomass burning OA by PMCAMx-SR during May 2008: (a) St. Petersburg (Russia), (b) Catania (Italy) and (c) Majden (FYROM).~~

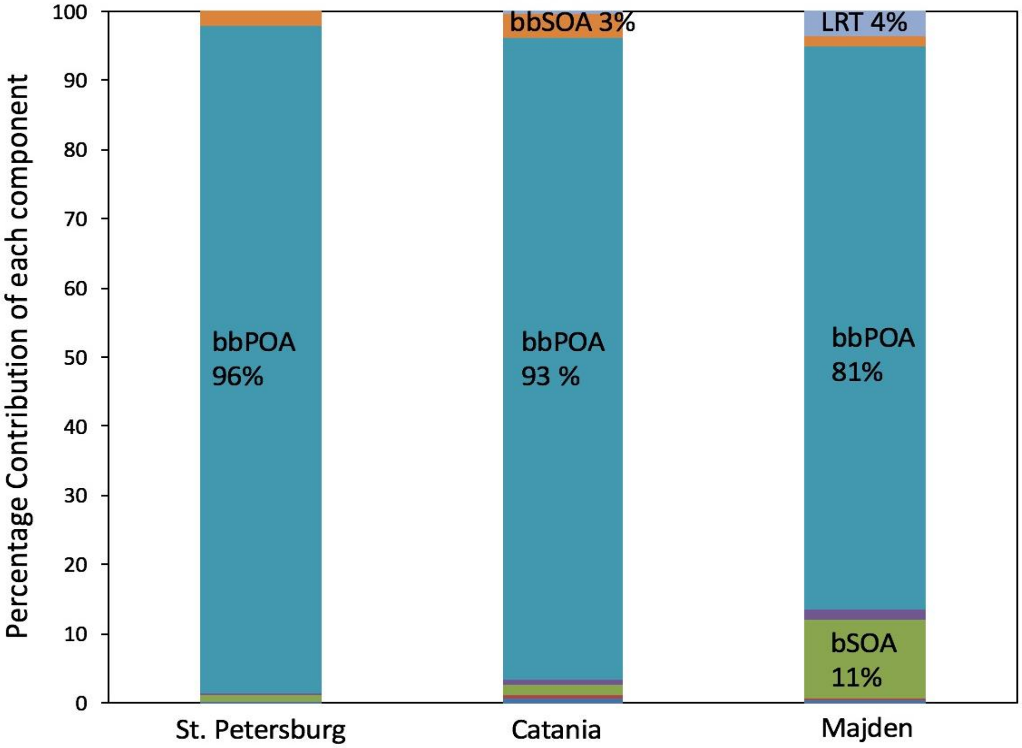


Figure 4~~5~~. Contribution of each OA component to the PMCAMx-SR bbPOA factor in St. Petersburg, Catania. and Majden during May 2008.

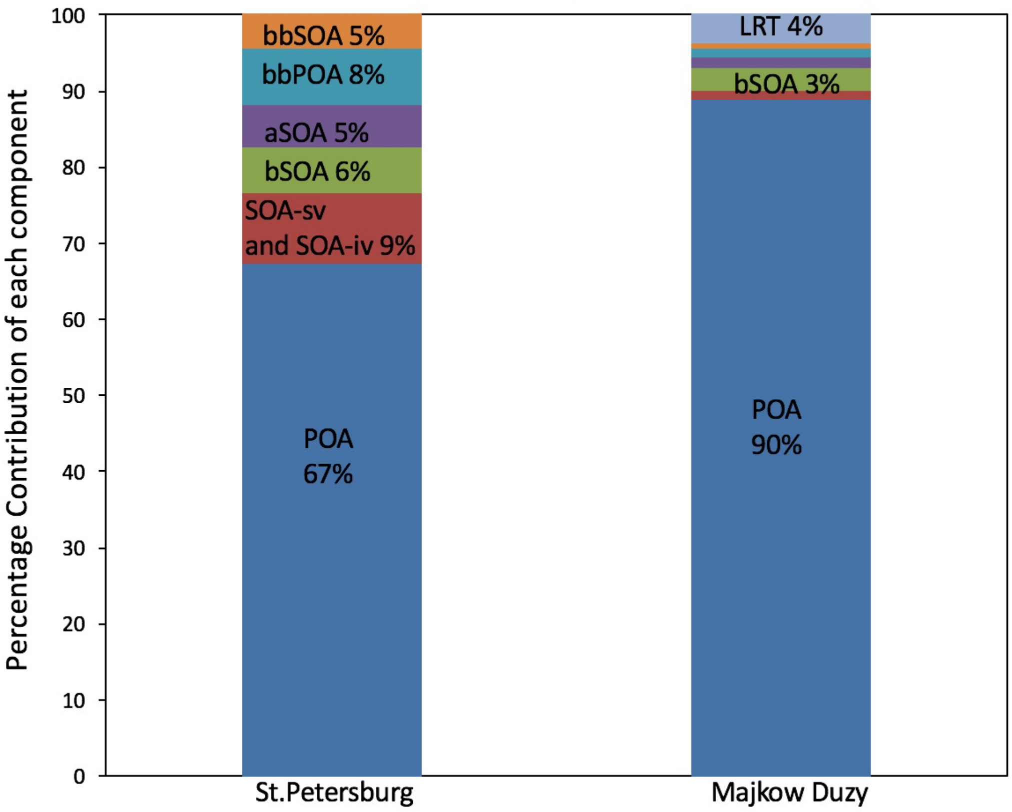


Figure 5~~6~~. Contribution of each OA component to the PMCAMx-SR PMF POA factor in St. Petersburg (Russia) and Majkow Duzy (Poland) during May 2008.

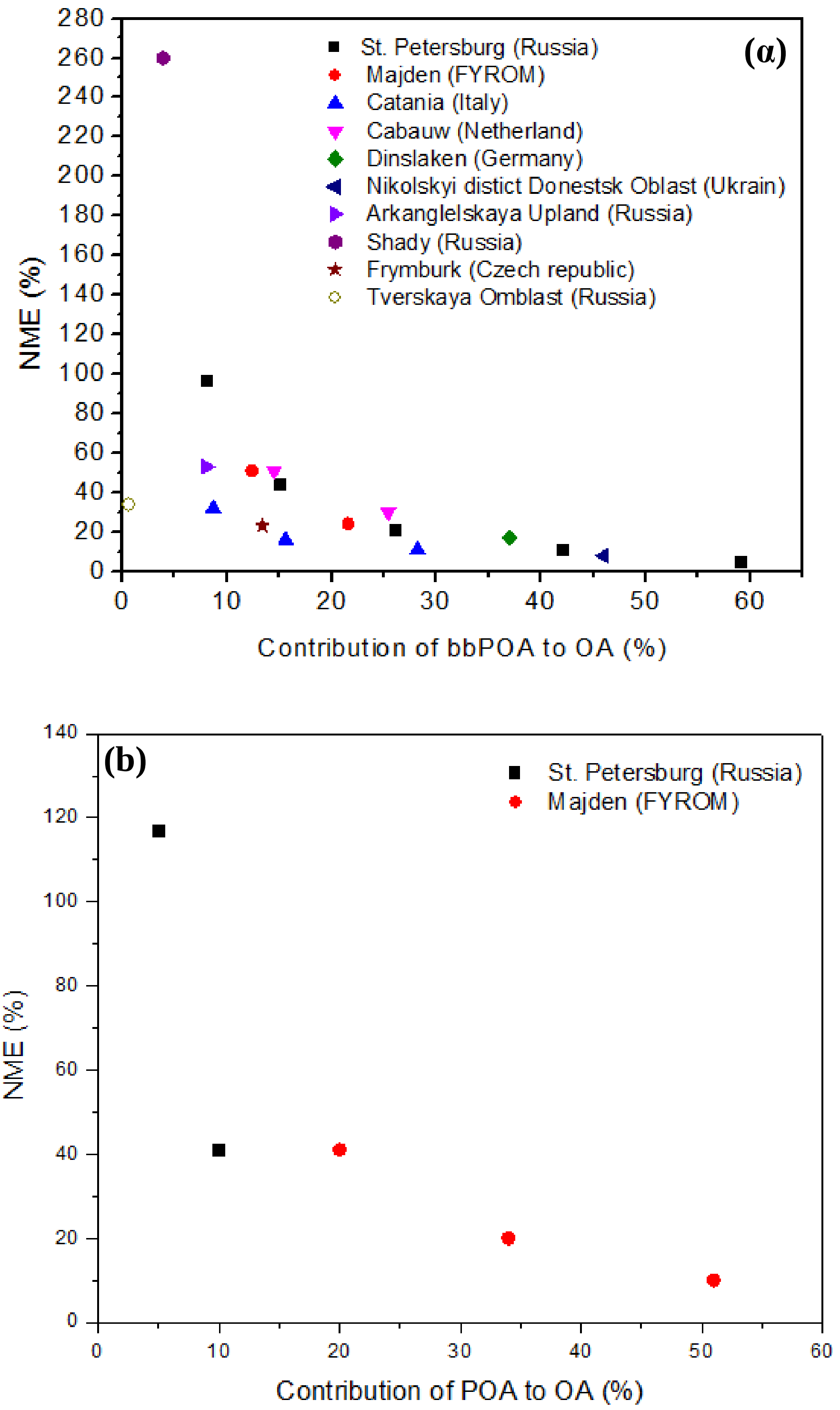


Figure 6~~7~~. PMF normalized error (%) for (α) bbPOA and (β) POA for various locations as a function of their contribution to OA.

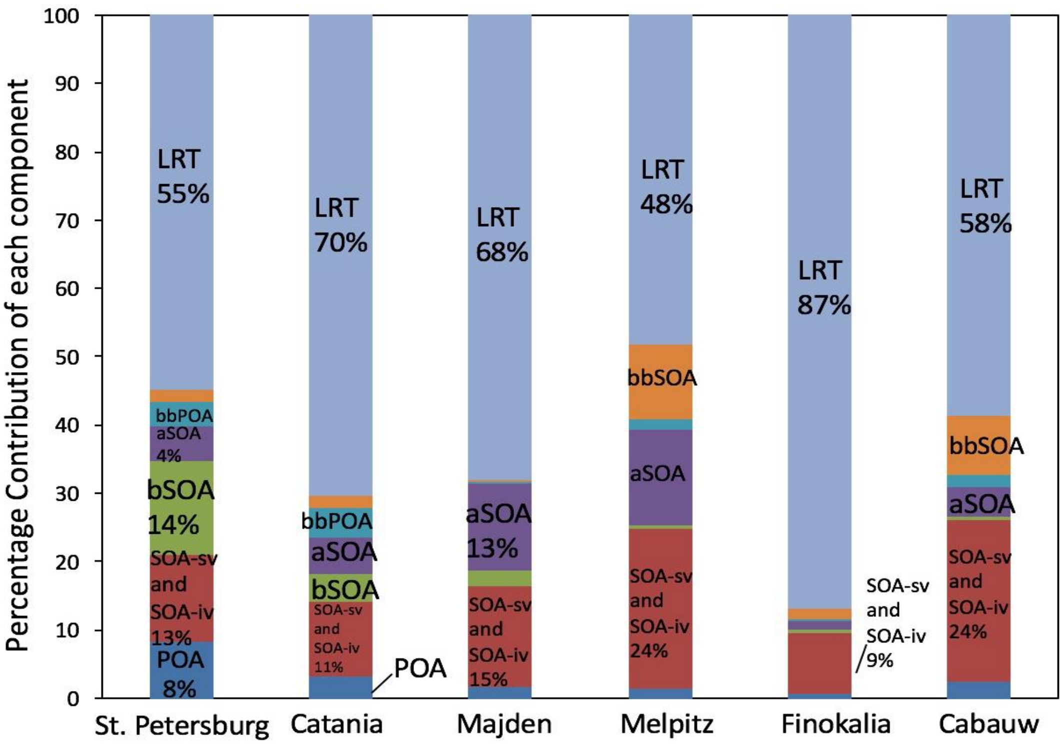


Figure 7~~8~~. Contribution of each OA component to PMCAMx-SR LRT factor in St. Petersburg, Catania, Majden, Melpitz and Finokalia during May 2008.

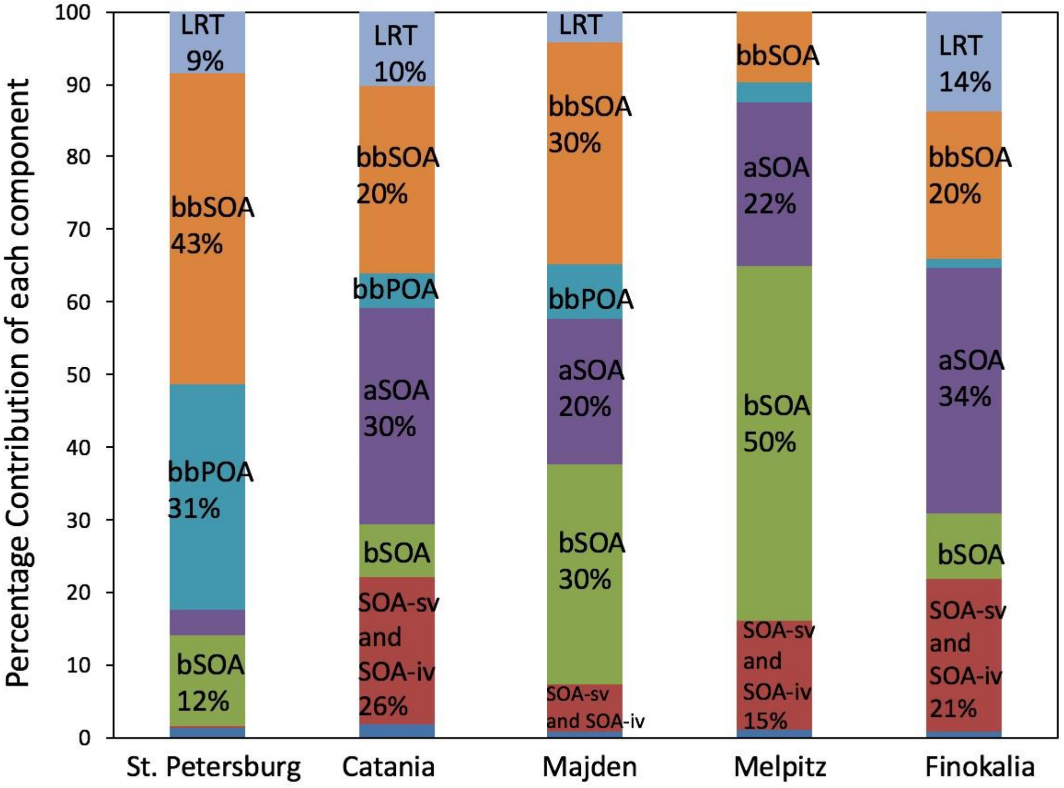


Figure 8~~9~~. Contribution of each OA component to the PMCAMx-SR SOA factor in St. Petersburg, Catania, Majden, Melpitz and Finokalia during May 2008.

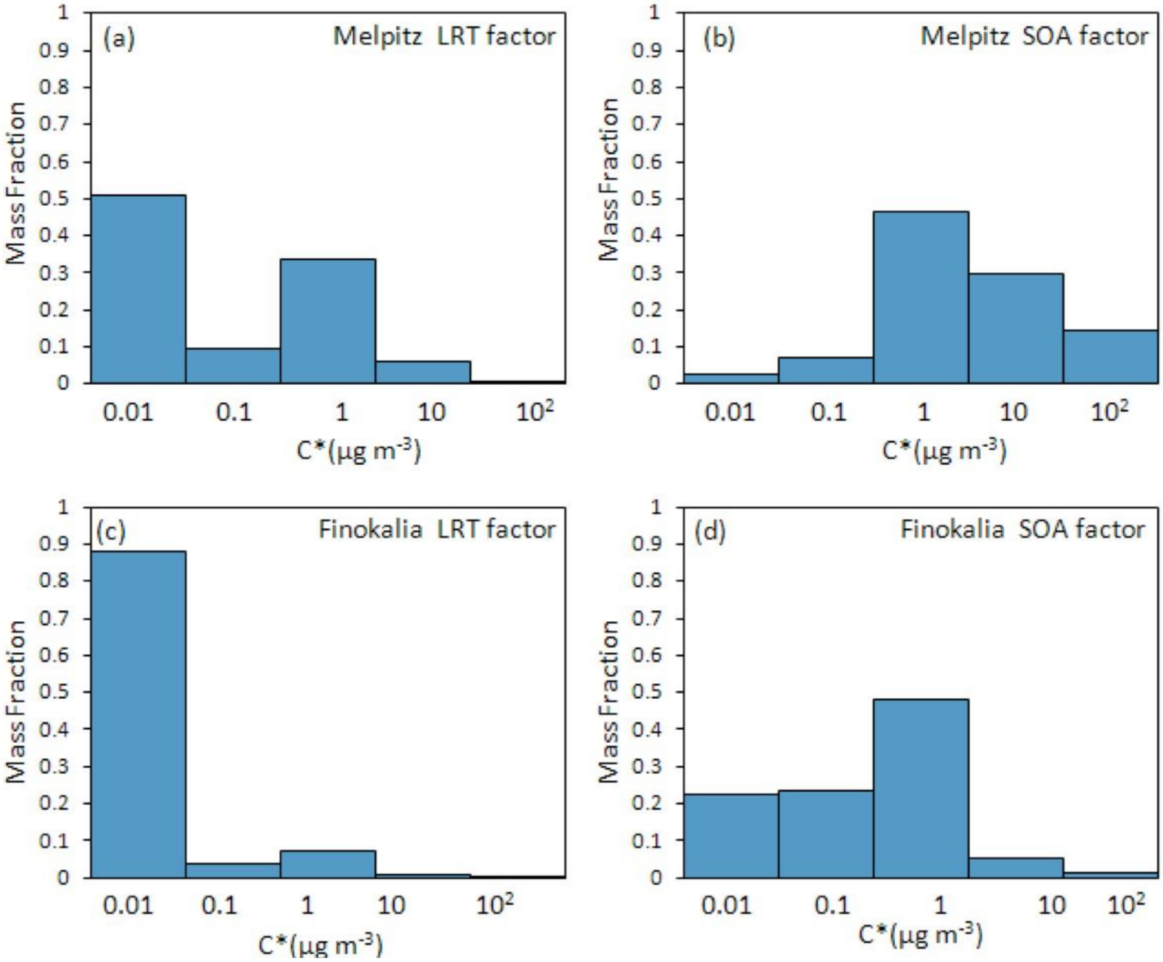
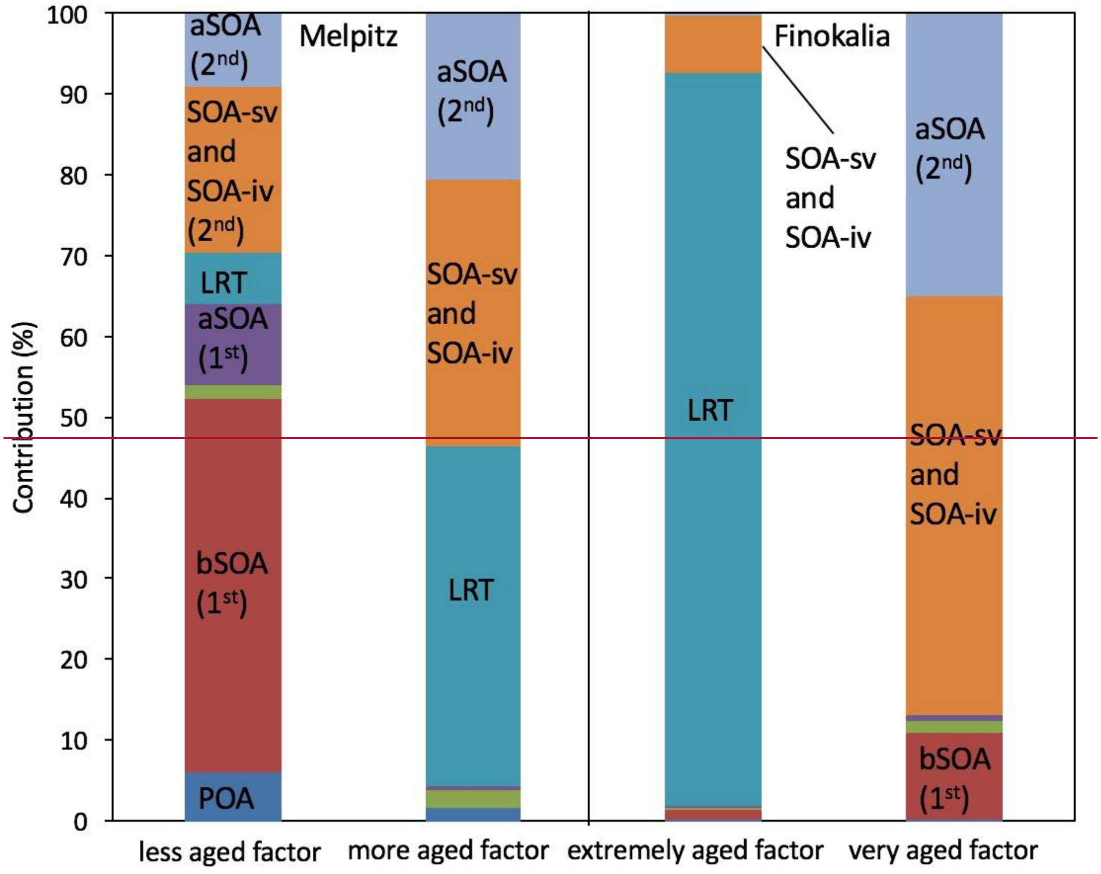
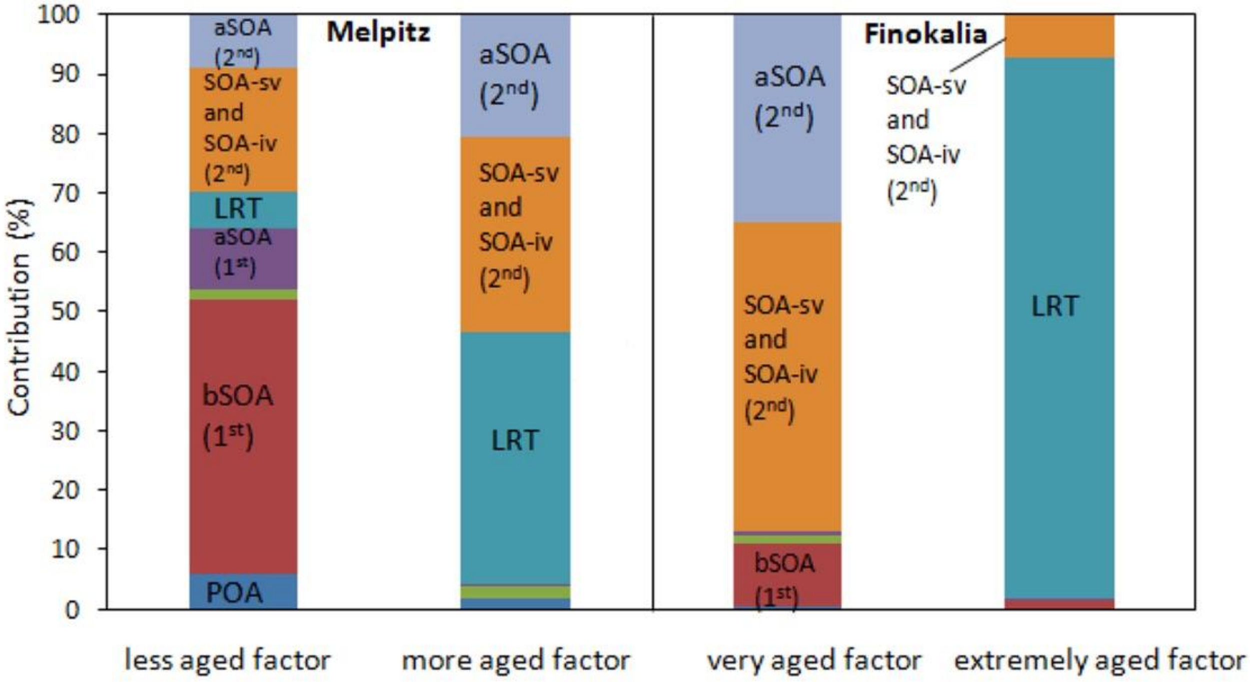


Figure 9~~10~~. Volatility distribution of the: (a) LRT factor in Melpitz, (b) SOA factor in Melpitz, (c) LRT factor in Finokalia, and (d) SOA factor in Finokalia.



Melpitz
Finokalia
Contribution (%)
0
10
20
30
40
50
60
70
80
90
100
aSOA (2nd)
SOA-sv and SOA-iv (2nd)
LRT
aSOA (1st)
bSOA (1st)
POA
aSOA (2nd)
SOA-sv and SOA-iv
LRT
LRT
SOA-sv and SOA-iv
aSOA (2nd)
SOA-sv and SOA-iv
bSOA (1st)
less aged factor
more aged factor
extremely aged factor
very aged factor



Melpitz
Finokalia
Contribution (%)
0
10
20
30
40
50
60
70
80
90
100
aSOA (2nd)
SOA-sv and SOA-iv (2nd)
LRT
aSOA (1st)
bSOA (1st)
POA
aSOA (2nd)
SOA-sv and SOA-iv (2nd)
LRT
aSOA (2nd)
SOA-sv and SOA-iv (2nd)
bSOA (1st)
SOA-sv and SOA-iv (2nd)
LRT
less aged factor
more aged factor
very aged factor
extremely aged factor

Figure 10~~1~~. Contribution of first generation and second plus later generations of SOA components to each factor in Melpitz and Finokalia during May 2008.