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# The Effect of the Averaging Period for PMF Analysis of Aerosol Mass Spectrometer Measurements during Off-Line Applications

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**Abstract.** Off-line Aerosol Mass Spectrometer (AMS) measurements can provide valuable information about the ambient organic aerosol in areas and periods in which online AMS measurements are not available. However, these offline measurements have low temporal resolution as they are based on filter samples collected usually over 24 hours. In this study we examine whether and how this low time resolution affects source apportionment results. We used a five-month period (November 2016-March 2017) of online measurements in Athens and performed Positive Matrix Factorization (PMF) analysis to both the original dataset, which consists of 30 min measurements, and to time averages from 1 up to 24 h. The 30 min results indicated that five factors were able to represent the ambient organic aerosol (OA): a biomass burning organic aerosol factor (BBOA) contributing 16% of the total OA, hydrocarbon-like OA (HOA) (29%), cooking OA (COA) (20%), more oxygenated OA (MO-OOA) (18%), and less oxygenated OA (LO-OOA) (17%). Use of the daily averages resulted in estimated average contributions that were within 8% of the total OA compared with the high resolution analysis for the five-month period. The most important difference was for the BBOA contribution which was overestimated (25% for low resolution versus 17% for high resolution) when daily averages were used. The estimated secondary OA varied from 35 to 28% when the averaging interval varied between 30 min and 24 h. The error for the low resolution analysis was much higher for individual days and its results especially for high concentration days are quite uncertain. The low resolution analysis introduces errors in the determined AMS profiles for the BBOA and LO-OOA factors but determines the rest relatively accurately (theta angle around 10 degrees or less).

## 1 Introduction

Exposure to high concentrations of particulate matter (PM) can lead to major health problems including stroke, heart disease and lung cancer (WHO, 2004; Pope and Dockery, 2006). Around 90% of the world population lives in places where air pollution exceeds the World Health Organization limits and more than 4 million people die every year due to ambient air pollution (WHO, 2018). To decrease the levels of PM it is necessary to identify its sources in each area and quantify their contributions.

https://doi.org/10.5194/amt-2022-100
Preprint. Discussion started: 22 April 2022


Atmospheric Measurement Techniques Discussions

Receptor models have been used for decades for the quantification of atmospheric aerosol sources (Hopke, 1991). Positive Matrix Factorization (PMF) (Paatero and Tapper, 1994) is the most widely used approach for the organic aerosol (OA) Aerosol Mass Spectrometer measurements. PMF constraints result in non-negative solutions, which make it suitable for the analysis of environmental data. PMF has been used in many studies (Ulbrich et al., 2008; Aiken et al., 2009; Docherty et al., 2011) in order to estimate the sources of the OA and it does not require a-priori information about the profiles. However, there are cases in which PMF can result in mixed or non-meaningful factors (Canonaco et al., 2021). In these cases the multilinear engine algorithm (ME-2) (Paatero, 1999; Canonaco et al., 2013) can be used. ME-2 has the advantage that pre-determined factors can be assumed by the user and, with a certain degree of freedom, will be part of the final solution (Crippa et al., 2014).

One of the challenges of PMF application on OA AMS spectra is that the factor profiles may change over time. This is especially true for oxygenated OA (OOA) factors (Freney et al., 2011; Dai et al., 2019; Via et al., 2021). When periods with different aerosol chemistry are mixed, such as summer with winter months, important information can be lost (Xie et al., 2013; Canonaco et al., 2015; Reyes-Villegas et al., 2016). For that reason many studies that examine long-term datasets break them up to monthly or seasonal subsets (Xu et al., 2015; Budisulistiorini et al., 2016; Hu et al., 2017) that are analyzed separately. The use of a rolling window has been proposed for the analysis of large datasets (Parworth et al., 2015; Chen et al., 2020; Canonaco et al., 2021) thus avoiding choosing periods by trial and error.

The robustness of the PMF results depends on the number of samples used; the relative errors increase as the sample dimension decreases (Hedberg et al., 2005). Typically at least 60-200 sets of observations are used for PMF analysis of individual aerosol components (Jaeckels et al., 2007). Hedberg et al. (2005) compared the results derived from 80 $PM_{10}$ measurements of 26 elements and from randomly reduced subsets, containing 85%, 70%, 50% and 33% of the initial samples. A five factor solution was determined in each case. The results of the analysis of the reduced subsets showed that the source contribution of each factor to the total OA differed by less than 10% with the contributions derived from the initial dataset. Zhang et al. (2009) analyzed a total of 273 samples for 46 VOCs, organic and elemental carbon and silicon. Multiple subsets, including approximately half of the observations (135 samples), 33% (90 samples) and 20% (54 samples) were also analyzed. The results of the 50 samples datasets had high relative standard deviations (above 50%) for the contribution of some factors with low OC concentrations. These suggest that the corresponding results were quite uncertain. There have been studies that attempted PMF analysis for PM elements using only 30-50 samples (Sunder Raman and Ramachandran, 2010; Tiwari et al., 2013; Manousakas et al., 2015). For example Manousakas et al. (2017) used a dataset of 55 samples with 22 elements and identified 6 factors. The solution was relative robust suggesting that the sample size was sufficient for the purposes of these studies.

Other studies have examined the source apportionment of different time resolution inputs of VOCs, metals, or combinations of inorganic ions with metals or VOCs with metals. Peng et al. (2016) measured 15 $PM_{2.5}$ metals, organic and elemental carbon and 6 inorganic ions with 1 h time resolution in Beijing, resulting in 528 samples. ME-2 was conducted at four temporal resolution settings (1, 2, 4 and 8 h) and a four factor solution was obtained in each case. The biggest discrepancy

https://doi.org/10.5194/amt-2022-100
Preprint. Discussion started: 22 April 2022


Atmospheric Measurement Techniques Discussions

among the contributions of each factor to the total $PM_{2.5}$ was observed for coal combustion which varied from 15% of the total $PM_{2.5}$ (for the 1 h) to 29% (for the 4 h); in the 8 h analysis it was 27%. Wang et al. (2018) examined the impact of time resolution on PMF results, by averaging the initial 512 1 h resolution samples of 20 PM components (13 elements, 4 inorganic components, OC, EC and $PM_{2.5}$ mass) to 4 h (145 samples) and 6 h (97 samples) time intervals. Even though the same eight factors were identified for every averaging interval, 3 of them showed large variation in the average contribution in the low resolution cases. Yu et al. (2019) used 1 h (N=6456) measurements of 16 metals and averaged them over 23 h (N=297). The 23 h PMF analysis overestimated the mass concentration for 2 out of the 6 factors, but gave consistent factor contributions with the 1 h solution.

Off-line AMS analysis was introduced by Daellenbach et al. (2016). Filter samples ($PM_1$, $PM_{2.5}$ and $PM_{10}$) are extracted in ultrapure water. The water extracts are filtered and aerosolized, thus converted to droplets which are dried and measured with an AMS. The 24 h average AMS spectra from the offline and the online analysis were highly correlated ($R^2$>0.97) (Daellenbach et al., 2016). The PMF results obtained from 24 h filter samples were very different from collocated on-line measurements, even though there were not such differences in the input spectra. It is not clear if discrepancies could be due to the temporal resolution of the analysis.

Even though there are studies which have examined the effect of time resolution for several chemical species such as metals and VOCs, it is not yet clear whether the low temporal resolution in the off-line AMS analysis introduces significant errors in the estimated contributions of different sources. To explore this we conducted PMF analysis for an ambient OA dataset averaged in different resolutions (from 1 h up to 24 h) and compared the results with the initial resolution of the dataset which was 30 min. The longer-term aim of this study is to characterize step by step the uncertainty of the PMF analysis of off-line AMS applications, neglecting at this stage the uncertainty arising from the various sampling and extraction artifacts.

## 2 Measurements and their PMF analysis

In this study, a dataset obtained by an Aerosol Chemical Speciation Monitor (ACSM) (Aerodyne Inc., USA) is used, operated at the National Observatory of Athens (NOA) at Thissio, in the center of Athens. The measurement resolution was 30 min. Measurements lasted one year, beginning in July 2016 and ending in August 2017.

For the PMF analysis the SoFi (Source Finder) version 6.1 graphic interface (Canonaco et al., 2013) was used. OA unit mass resolution spectra (*m/z* 12-125) were analyzed. The error matrix was weighted using a step function, as proposed by Paatero and Hopke (2003), and a cell-wise signal-to-noise ratio (S/N) was calculated (Brown et al., 2015). “Bad” signals with S/N below 0.2 were down-weighted by a factor of 10, “weak” signals with S/N between 0.2 and 1 were down-weighted by a factor of 2 and the $CO_2$ related variables (*m/z* 16, 17, 18, 44) were also down-weighted by a factor of 2 (Ulbrich et al., 2009). The minimum *Fpeak* value was -1 and the maximum 1. The *Fpeak* step was 0.1. The optimum *Fpeak* was chosen each time based on the physical meaning of the factors, the resulting spectral profiles and their diurnal variation of the factor levels.

https://doi.org/10.5194/amt-2022-100
Preprint. Discussion started: 22 April 2022


Atmospheric Measurement Techniques Discussions

## 3 Results and discussion

### 3.1 Monthly PMF analysis of the full annual dataset

The full one-year dataset was initially analyzed by month at the highest time resolution, which was 30 min. The contribution of each factor to the total OA for each month is shown in Fig. 1. The PMF analysis for the summer months (June, July and August) showed that four factors could represent the ambient OA: two primary (COA and HOA) and two secondary (MO-OOA and LO-OOA). Four factors were also identified for the first two autumn and the last two spring months. The PMF analysis for December, January and February showed the presence of an extra BBOA factor. The same additional factor was found for November and March. These results are consistent with those of Stavroulas et al. (2019) where PMF analysis was done separately for a "cold period" (November to March) and a "warm period" (May to September). Again four factors (HOA, COA, MO-OOA, and LO-OOA) were found for the "warm period", while in the "cold period" an additional BBOA factor was identified.

The subset that was used in this study was the five-month cold period, beginning at November 1 2016 and ending at March 18, 2017, resulting in a set of 6150 30-min samples. This period was chosen, because of the presence of the BBOA factor in the PMF analysis, which is an additional primary factor. The average organic mass concentration for this cold period was 9.2 μg $m^{-3}$ with a maximum concentration of 201 μg $m^{-3}$ (Fig. 2). From now on all the results will refer to this cold time period.

### 3.2 High temporal resolution PMF analysis

The 6150 30-min measurements during the cold period were analyzed together. Five factors could represent the variation of the organic aerosol ACSM spectra based both on the residuals and the physical meaning of the solutions (Fig. S1-S3). Three of them were primary (HOA, COA and BBOA) contributing 65% to the total OA, and two were secondary (MO-OOA and LO-OOA) with a contribution equal to 35%. The same result for all practical purposes was observed from the analysis of the measurements during each month separately, with an average primary contribution of 63%. We will focus first on the analysis of the full dataset (all months together) and then discuss the analysis of the data of each month separately.

HOA was the biggest contributor (29%) to the total OA for the cold period. The average HOA concentration peaked at 9:00 local time (LT) (Fig. 3), which is consistent with the local rush hour. Its mass spectrum was characterized by *m/z's* 41, 43, 55 and 57 (Fig. S4). COA was the second biggest contributor to the total OA, representing 20% of the total OA. The COA mass spectrum had a strong peak at *m/z* 41, and a high ratio of *m/z* 55/57. This high ratio characterizes COA emissions in urban areas (Sun et al., 2011). BBOA represented 16% of the total OA. Its maximum 30 min concentration reached 58 μg $m^{-3}$ (Fig. S5). The distinguishing feature of BBOA is the presence of strong signals at *m/z's* 60 and 73 (Ng et al., 2011b). The diurnal profile of the BBOA showed an increase at 18:00 LT reaching a peak at 23:00 LT. This 18:00-23:00 LT period is consistent with the times that fireplaces are used in Athens, a common indoor heating process in Greece during the last decade. MO-OOA, representing 18% of the total OA, had little average diurnal variation, and an average concentration of 1.7 μg $m^{-3}$. On

https://doi.org/10.5194/amt-2022-100
Preprint. Discussion started: 22 April 2022


Atmospheric Measurement Techniques Discussions

the other hand, LO-OOA (17% of the total OA) increased during night-time when primary OA also increased. This is consistent with local night time production during wintertime (Kodros et al., 2020). The PMF results from this study agreed (within 20%) with the Stavroulas et al. (2019) unconstrained PMF analysis. Stavroulas et al. (2019) used as inputs in their analysis factor profiles for the BBOA, COA and HOA allowing ME-2 a certain degree of freedom around these inputs. In the present study the unconstrained solution is used in order to avoid the additional complexity that the use of external factors may introduce. Detailed comparisons between the unconstrained solutions of the studies can be found in the SI (Figs. S6 and S7).

### 3.3 Comparisons between PMF results at different temporal resolution

The goal of this study is to examine whether the PMF results change as the sampling time resolution decreases. For this reason we calculated the 1, 2, 4, 6, 8, 10, 12 and 24 h averages of the measured OA spectra and performed PMF analysis in each new dataset. The number of samples used in each averaged dataset were above 100 in each case (Table S1). Five factors were able to explain the OA variation in all cases. The estimated primary factor (HOA, COA and BBOA) contribution to the total OA ranged from 72% (at 24 h) to 58% (at 10 h resolution). The 30 min resolution analysis suggested that 65% of the total OA was primary (Fig. 4).

The HOA contribution to the total OA ranged from 29% (30 min) to 23% (daily resolution) (Fig. 5). The 30 min COA contribution was 20% of the OA. The minimum COA observed was 19% (4 h) and the maximum 25% (daily resolution). The BBOA contribution varied the most among the primary factors and ranged from 15% (1 h) to 24% (daily resolution). In the 30 min solution the BBOA contribution was 16% of the OA.

In the 30 min analysis the estimated LO-OOA contribution to the total OA was 17%. The LO-OOA showed a quite sensitive and unstable behavior, as it ranged from 10% (6 h) to 21% (2 h), and for the daily resolution was 13%. The 30 min MO-OOA was 18% of the OA and ranged from 15% (daily resolution) to 24% (6 h).

The variation of the spectra of the various factors resulting from the analysis at different averaging periods was quantified using the theta angle (Kostenidou et al., 2009). The highest angle calculated between the different resolution spectra with the 30 min ones for the COA was 26° (for the 6 h resolution). For HOA the highest angle was 19° (for the 10 h resolution) and for BBOA 22° (daily resolution) (Fig. 6). This indicates that in these cases the mass spectra were quite different from the 30 min spectrum. Detailed information about the spectral comparisons can be found in the SI (Fig. S8).

The MO-OOA spectrum remained relatively similar to the 30 min one for all resolutions, with the highest angle being 11° (for daily resolution). The MO-OOA factor location (Fig. 7) in the $f_{44}$ vs $f_{43}$ plot (Ng et al., 2011a) tended to move down approaching the LO-OOA factor as the temporal resolution was decreased. The LO-OOA spectrum was the most variable varying by as much as 30° from the high temporal resolution one and moving upwards in the plot. The MO-OOA O:C decreased from 1.09 to 0.88 as the time resolution decreased. The LO-OOA O:C increased from 0.32 for the 30 min resolution to 0.6 for the daily resolution (Fig. S9). This change in the LO-OOA spectrum and contribution appears to be one of the major effects of the PMF analysis time resolution

https://doi.org/10.5194/amt-2022-100
Preprint. Discussion started: 22 April 2022


Atmospheric Measurement Techniques Discussions

### 3.4 Analysis of the 24 h resolution results for each day

The daily resolution was the lowest resolution used in this work and is the usual resolution for off-line AMS analysis. The number of samples in this case was 127. In the 24 h solution the primary factors represented 72% of the total OA compared to 65% for the 30 min. So the use of the daily resolution measurements does not introduce significant errors in the primary/secondary OA split of the AMS analysis on average. While the ability of the low temporal resolution results to determine average contributions during the study period is encouraging, it is interesting to examine its performance for individual days. We estimated the daily average concentrations of the concentrations of the five factors from the 30 min analysis and we compared them with the results of the 24 h analysis for each day (Fig. 8).

For HOA the results of the two approaches were in encouraging agreement during most of the days and were well correlated ($R^2$=0.96). The tendency of the 24 h analysis to underestimate the HOA was evident during most days. During some days with relatively low HOA levels (below 2 μg $m^{-3}$) there were significant errors with the 24 h analysis estimating practically zero HOA and seriously underestimating its levels. Despite these discrepancies a relative good consistency in the estimates of the two approaches for the HOA role is observed, as the 30 min solution HOA (29% of the total OA) agrees well with that estimated from the 24 h resolution (23%).

The behaviour of the low temporal resolution PMF analysis for the COA was the opposite of that for the HOA. The COA was systematically overestimated during the high COA concentration (above 4 μg $m^{-3}$) periods (Fig. 8). In these days the 24 h COA resolution results were as much as two times higher than the 30 min results. For example, the highest COA concentration estimated by the high resolution analysis was 5.7 μg $m^{-3}$ on November 5. The low resolution COA for that day was 11.2 μg $m^{-3}$. On the other hand, the low resolution analysis tends to underestimates the COA during most of the days with COA levels below 2 μg $m^{-3}$ resulting in a relatively small overprediction (25% versus 20%) of its average contribution to OA during the full period.

The BBOA concentration was overestimated by the low resolution analysis by 20-30% at days with high concentrations (BBOA above 5 μg $m^{-3}$) (Fig. 8). The highest discrepancy was observed on January 2, which was the day with the highest BBOA concentration in the five month period (13 μg $m^{-3}$). The low resolution BBOA was 1.8 times higher than the high resolution at that day. At the same day the low resolution LO-OOA was underestimated (9.7 μg $m^{-3}$ for the high resolution results and almost zero for 24 h). These discrepancies were quite systematic ($R^2$=0.95) and resulted in an overestimation of the BBOA for the full period by the low resolution approach (24% of the OA versus 16% for the 30 min analysis). So at least for this dataset the use of the daily resolution leads to a systematic overestimation of the BBOA during most days.

Despite the discrepancies, the results of the two approaches for the primary factors were relatively well correlated with the $R^2$ varying from 0.82 for the COA to 0.96 for the HOA. This was not the case with the secondary factors where the $R^2$ between the results of the 30 min and 24 h analysis for the 127 daily data points was 0.24 for the LO-OOA and 0.32 for the MO-OOA. This underlines the sensitivity of the LO-OOA/MO-OOA split to the temporal resolution used for the analysis.

https://doi.org/10.5194/amt-2022-100
Preprint. Discussion started: 22 April 2022


Atmospheric Measurement Techniques Discussions

Despite these discrepancies for the daily results, the averages for the study period were relatively consistent (less than 5% of the OA) for the two analyses. The 24 h MO-OOA contribution was 15%, while the 30 min was 18%, and the 24 h LO-OOA contribution to the total OA was 13% while in the 30 min analysis it was 17%.

The factor profiles for the low and high temporal analyses are compared in Fig. S8. The spectra for HOA (7 degrees), MO-OOA (11 degrees) and COA (13 degrees) are quite consistent with each other and appear to be less sensitive to the temporal resolution of the analysis. On the other hand, there are significant differences in the spectra for BBOA (22 degrees) and LO-OOA (30 degrees) that are clearly a lot more sensitive.

### 3.5 Analysis of month-long datasets

Our analysis so far has focused on the effects of the temporal resolution for the full data set, that is all five months of a period with similar characteristics and sources together. For the 24 h analysis there were 127 samples using for the PMF. Certain field campaigns last a lot less than five months, so in this section we examine the analysis of the data of each month separately from the rest. For the 24 h analysis, this involves 28-31 samples for November to February and only 17 samples for March (due to missing data for technical reasons). So March is an interesting test case because the set of data is probably too small for such a PMF analysis. A five factor solution was obtained for each month in the 24 h resolution analysis.

The primary/secondary split calculated for the four months with complete data sets for the 24 h resolution was quite consistent (differences less than 10% of the OA) (Fig. 9). For March, the existence of only 17 data points resulted in significant error, as expected, with the 24 h resolution analysis estimating that 34% was primary, while the 30 min analysis estimate was 58%. So the 30 data points appear to be sufficient in this case, but the 17 produced erroneous results at least for the March conditions.

The results for the monthly average contribution (using only the 28-31 data points) of the various factors are quite encouraging (Fig. 10). The estimated BBOA contribution differed by 5% or less. The differences in HOA were a little higher, but still less than 10% of the total OA. A little, higher discrepancies were found for COA especially in November and December. For example, during November the COA was 23% of the OA according to the 30 min analysis and 34% based on the 24 h results.

The estimates of the contributions of the secondary factors had the highest discrepancies differing by as much as 13%. In general, there was better agreement for the sum of the OOA factors than for their individual values. For the MO-OOA the highest discrepancy was observed in December, in which the two resolution results differed by 10% (20% for the 30 min results and 10% in the daily resolution). The LO-OOA highest difference was 13% and was found for January during which the 30 min LO-OOA was 17%, while the 24 h was 30% of the OA.

During March the use of the small dataset with 24 h resolution, resulted in significant underprediction of the BBOA, underprediction of the COA and significant overprediction of the MO-OOA (Fig. 10) .This indicates that a 24 h sample size of 17 days will result in significant errors in five factor solutions in periods like March which is also at the end of the heating period.

https://doi.org/10.5194/amt-2022-100
Preprint. Discussion started: 22 April 2022


Atmospheric Measurement Techniques Discussions

## 4 Conclusions

In this study the impact of the time resolution in the PMF results of an ACSM was examined using data from an urban site in Athens during a relatively cold period. During this period the OA had both primary sources (transportation, biomass burning and cooking), but also a significant secondary component. Analysing the full data set (127 days) together, the same number of factors were found for each data averaging interval (30 min, and 1 , 2 , 4 , 6 ,8, 10, 12, 24 h): three primary and two secondary.

The average contribution to the total OA of each factor varied within 8% between the lowest and the highest temporal resolution results. This suggests that even the lowest resolution of 24 h samples often used for offline AMS analysis can provide valuable insights about the secondary OA and the major sources of the primary OA for a multi-month period. The improvement of the results going from 24 h to 12 h was marginal, suggesting that for at least this five-month period little would be gained by doubling the number of samples from 127 to 254.

The highest discrepancy between the 30 min and 24 h analysis results was found for BBOA. The low temporal analysis overestimated BBOA by 8% of the OA (24% for the 24 h versus 16% for the 30 min). One should note, that the same difference can be viewed as a 50% overestimation of the BBOA contribution. However, the accuracy of even the 30 min estimates is expected to be low, so this 50% overestimation may be misleading. The tendency the 24 h analysis to overestimate BBOA in this dataset is noteworthy and should be compared with the results of similar analysis in other locations. The discrepancies for the other OA components were an underprediction of the HOA by 6% of the OA by the 24 h analysis (23% versus 29% for the 30 min), an overprediction of the COA by 5% (25% versus 20% for the 30 min), an underprediction of the LO-OOA by 4% (13% versus 17%) and an underprediction of the MO-OOA by 3% (15% versus 18%). The tendency towards a small underprediction of the secondary OA should also be examined in future studies.

The discrepancies between the results of the 24 h and the 30 min analysis increased when the PMF analysis was performed for just one month (28-31 days) assuming that only one month of daily filter samples was available for off-line AMS analysis. However, the differences of the estimated contributions of the various factors remained below 13% of the total OA. This suggests that even one month of daily samples can provide valuable insights about the OA components and sources on average. Of course, the uncertainty is higher compared to multiple-month data sets.

The uncertainty of the off-line AMS analysis will be a lot higher if one focuses on individual days, even if there are months of available data. Discrepancies of a factor of two were observed for several factors when the 30 min and 24 analyses were compared. These high discrepancies were observed not only for relatively clean days, but some of the days with the highest concentrations of the BBOA and COA factors. This suggests that the off-line AMS results are quite uncertain for specific days.

Finally, the factor profiles determined by the 30 min and 24 h resolution analysis were relatively similar for HOA (theta angle 7 degrees), but there were some differences for MO-OOA (11 degrees) and COA (13 degrees). There were significant differences in the spectra for BBOA (22 degrees) and LO-OOA (30 degrees).

https://doi.org/10.5194/amt-2022-100
Preprint. Discussion started: 22 April 2022


Atmospheric Measurement Techniques Discussions

*Data availability.* All the PMF results are available in https://zenodo.org/record/6477157#.YmJsFVBBxkw.

*Supplement.* The supplement related to this article is available at:

*Author contributions.* CV and SNP designed the study and wrote the paper. CV did the corresponding PMF analysis presented here. IS and NM obtained and provided the ACSM data. All authors contributed to the interpretation of the results and edited the manuscript.

*Competing interests*. The contact author has declared that neither they nor their co-authors have any competing interests.

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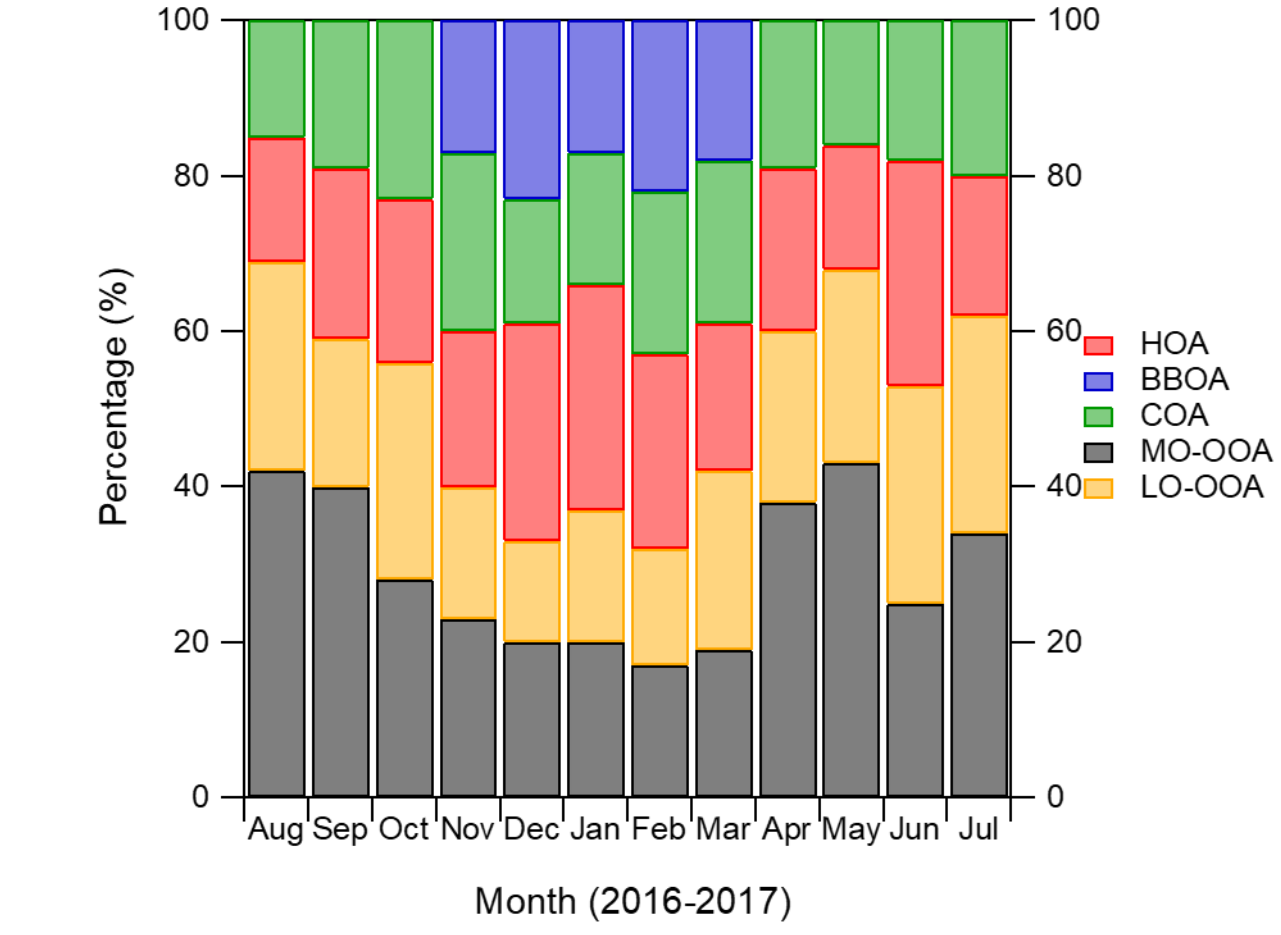


**Figure 1:** Fractional contribution of each factor to the total OA for the PMF analysis of each month separately. The 30 min data set was used for this analysis.

https://doi.org/10.5194/amt-2022-100
Preprint. Discussion started: 22 April 2022


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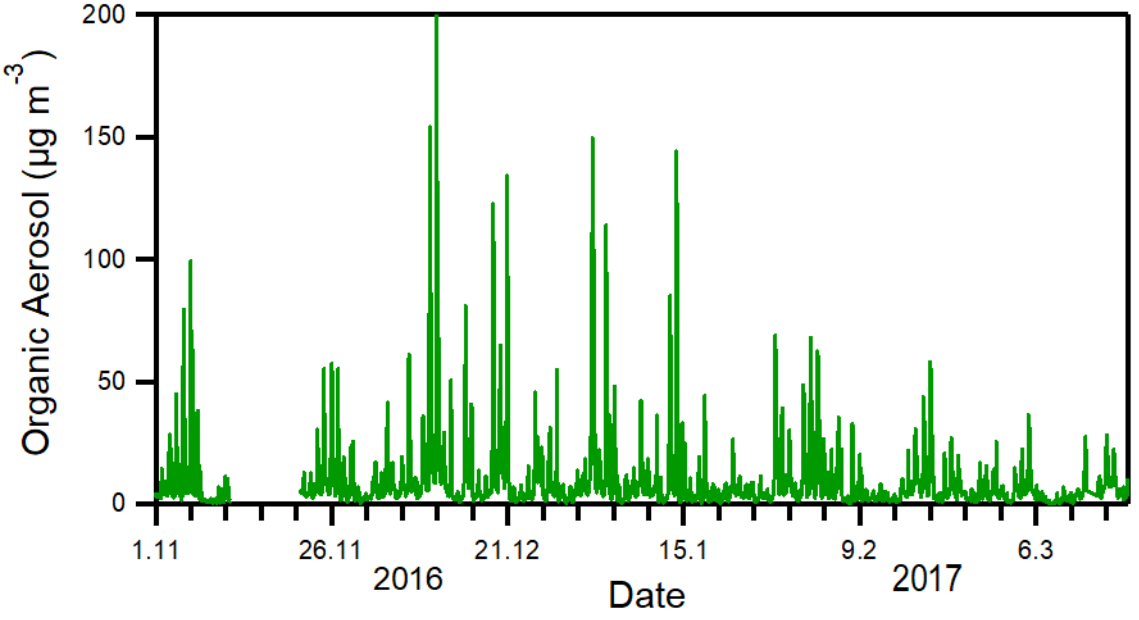


**Figure 2:** Organic aerosol concentrations measured by the ACSM in the center of Athens for the November-March cold period analyzed in this work. The time resolution is 30 min.

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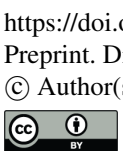
Preprint. Discussion started: 22 April 2022

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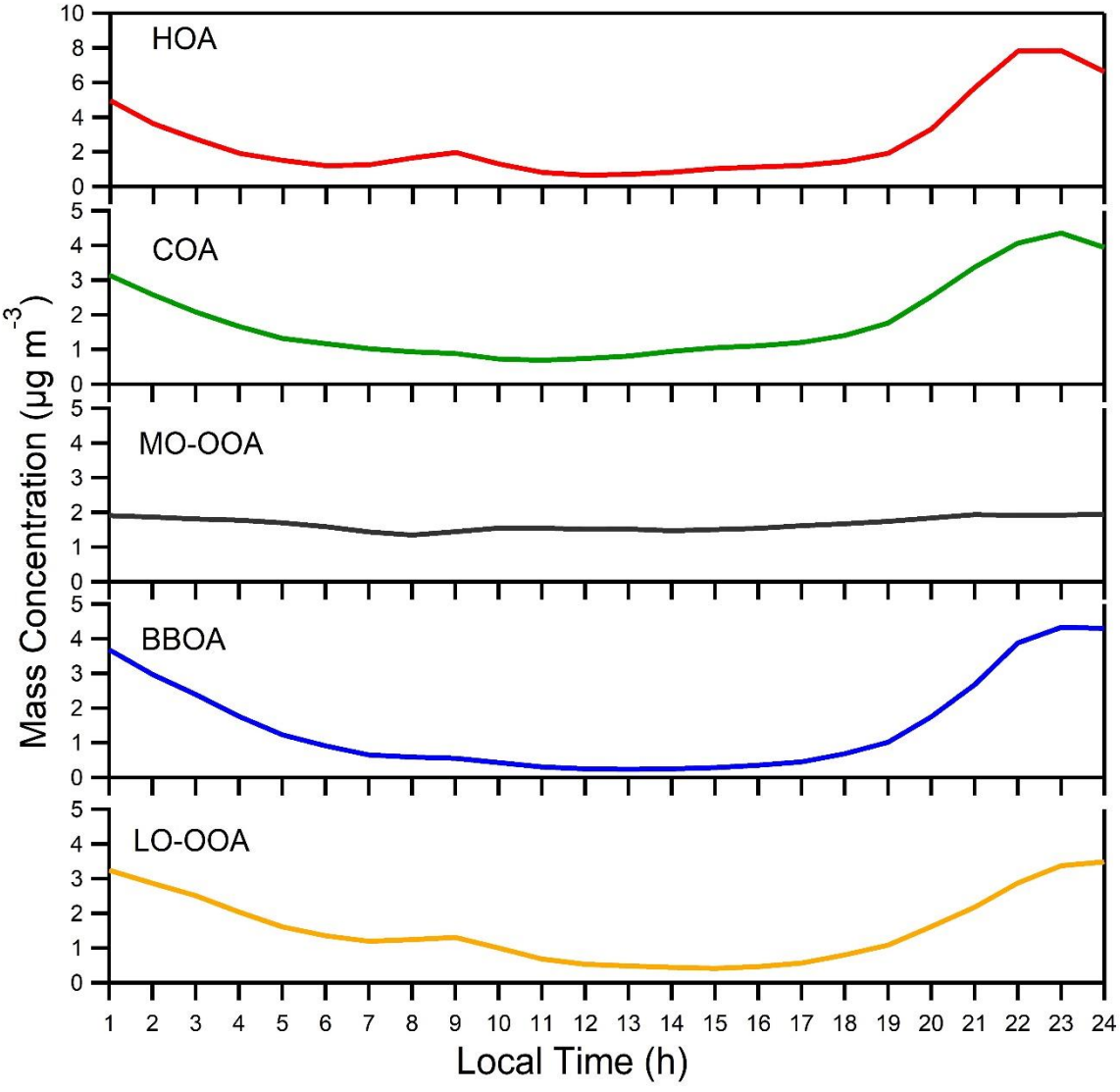


**Figure 3:** Average diurnal profiles for the five factors derived from the 30 min time resolution PMF results during the cold period (November 2016- March 2017). Different scales are used for the HOA and the rest of the OA components.

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Preprint. Discussion started: 22 April 2022


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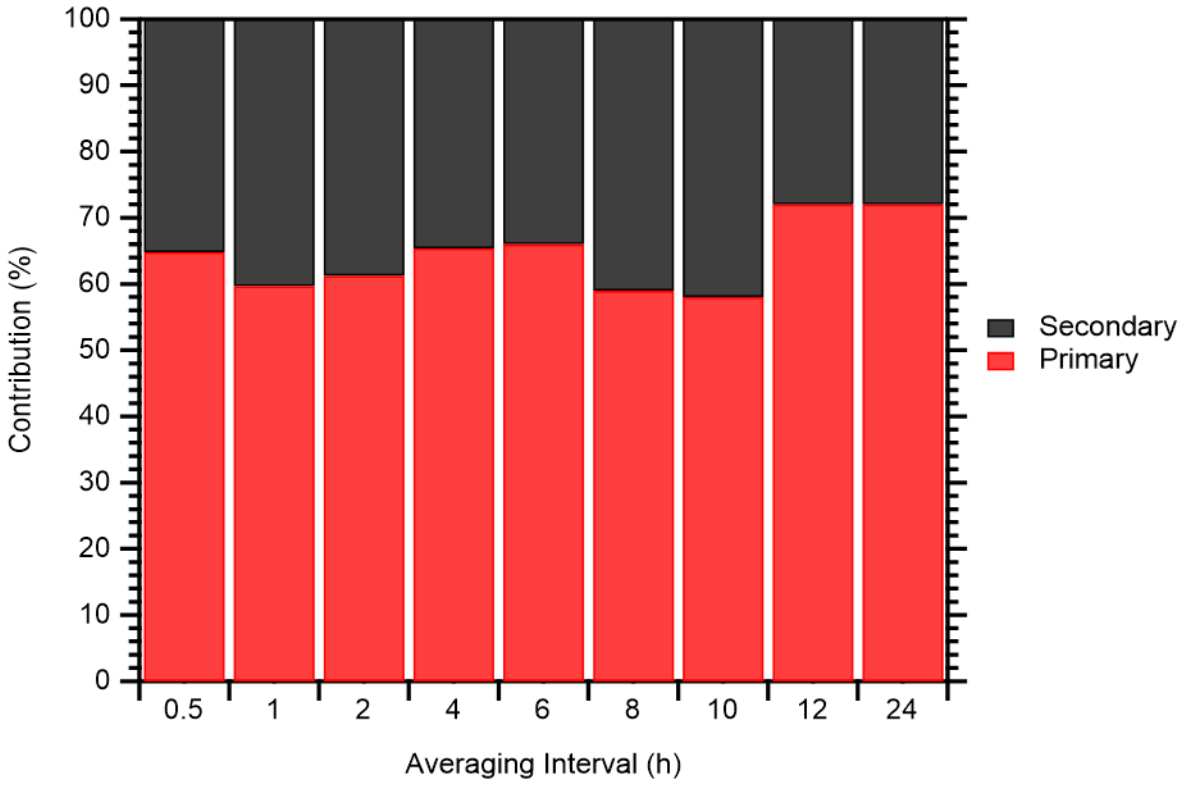


**Figure 4:** Contribution of the sum of primary factors (HOA, COA and BBOA) and the sum of secondary factors (MO-OOA, LO-OOA) to the total OA for the various averaging intervals for the cold period.

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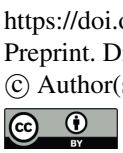
Preprint. Discussion started: 22 April 2022

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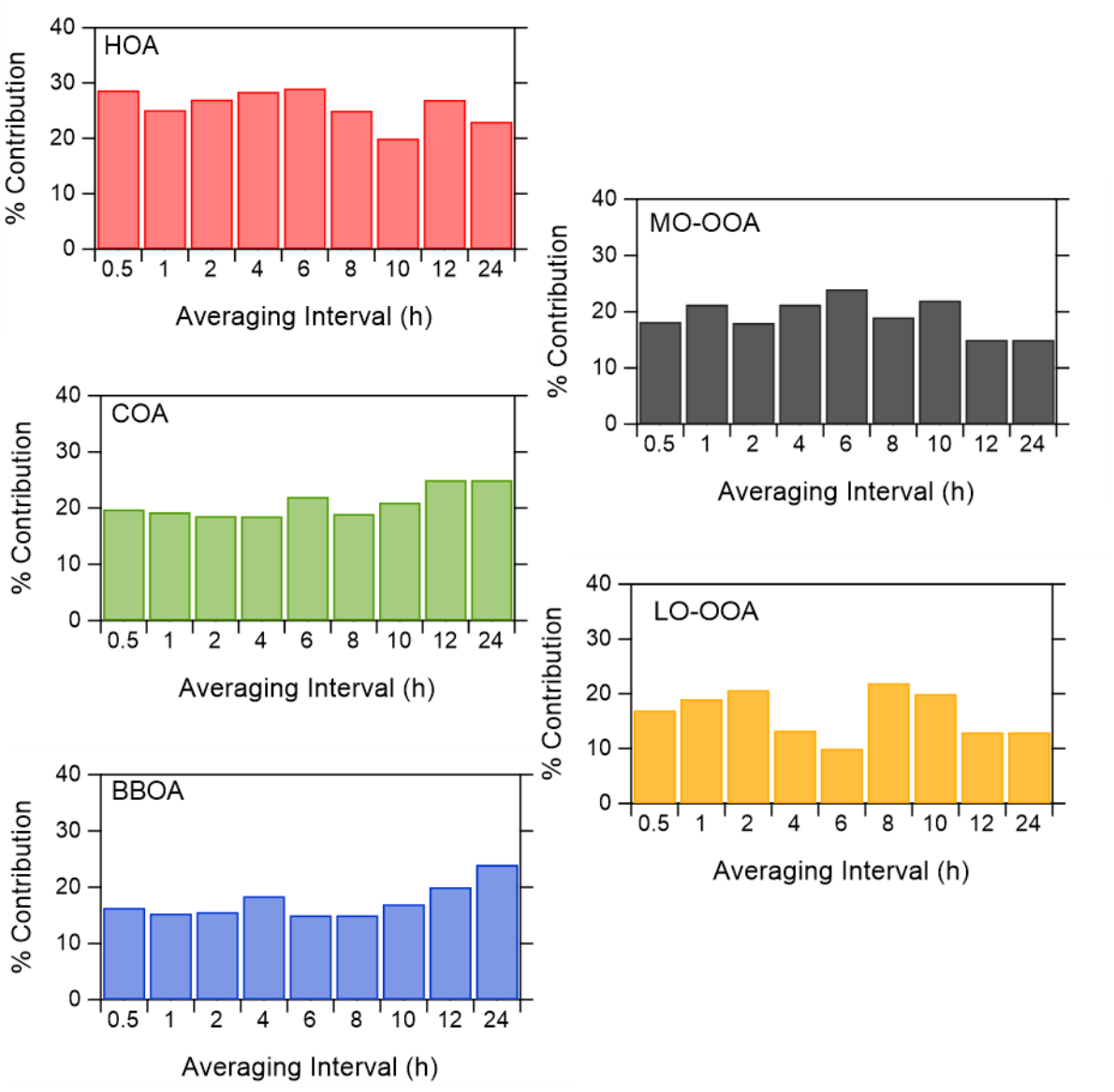


**Figure 5:** Contribution of each factor to the total OA for the different time resolutions.

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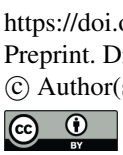

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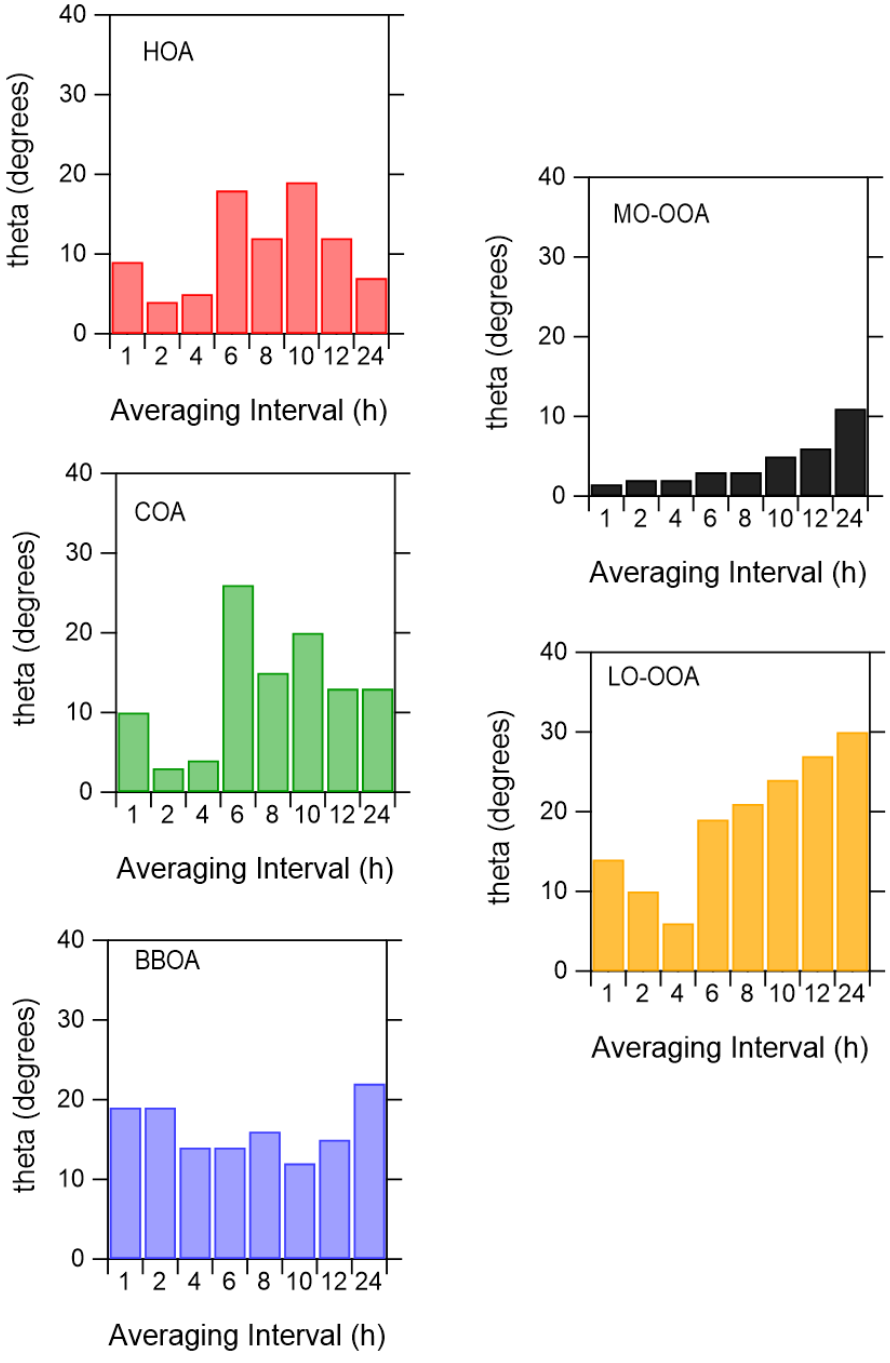


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**Figure 6:** Theta angle between the spectra derived from the 30 minutes PMF analysis and the spectra derived from the analysis at different time resolution.

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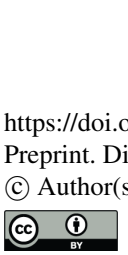
Preprint. Discussion started: 22 April 2022

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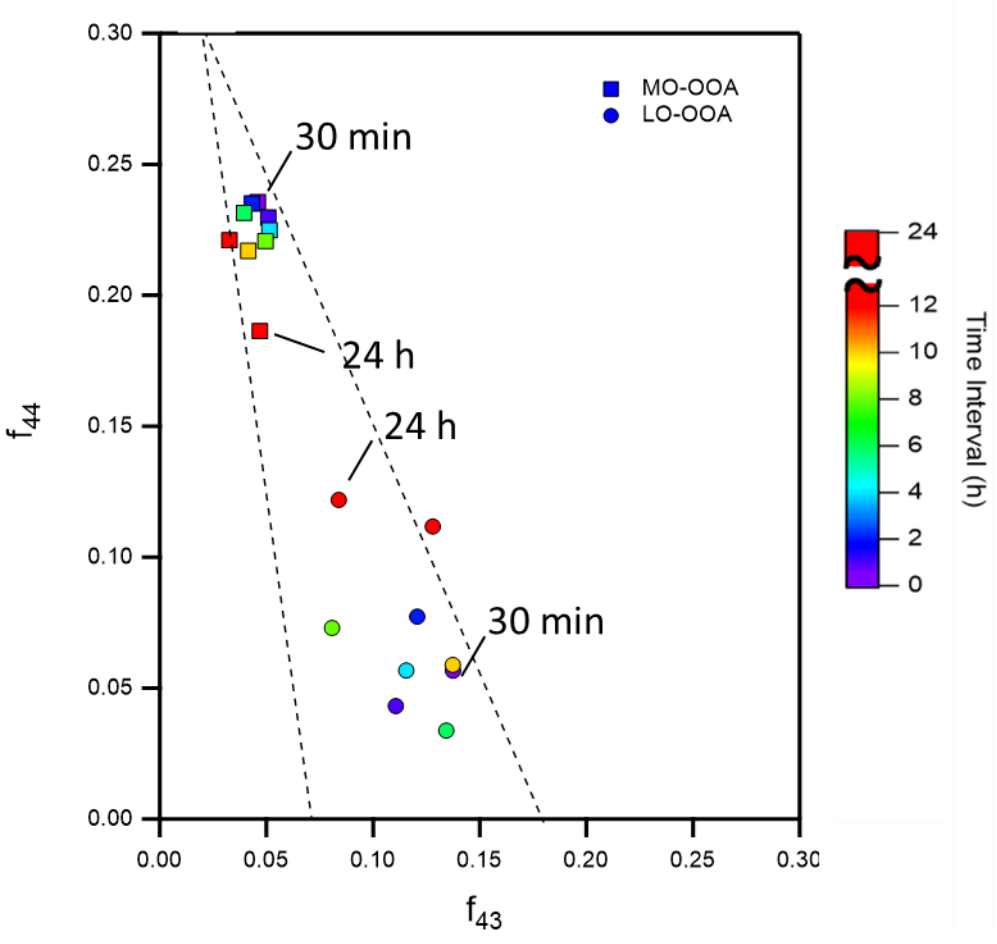


480 **Figure 7:** *f44* vs *f43* triangle plot of the two secondary factors for the different time intervals of the PMF analysis. The LO-OOA is shown with circles and the MO-OOA with squares. The results of the 30 min and the 24 h analysis are highlighted.

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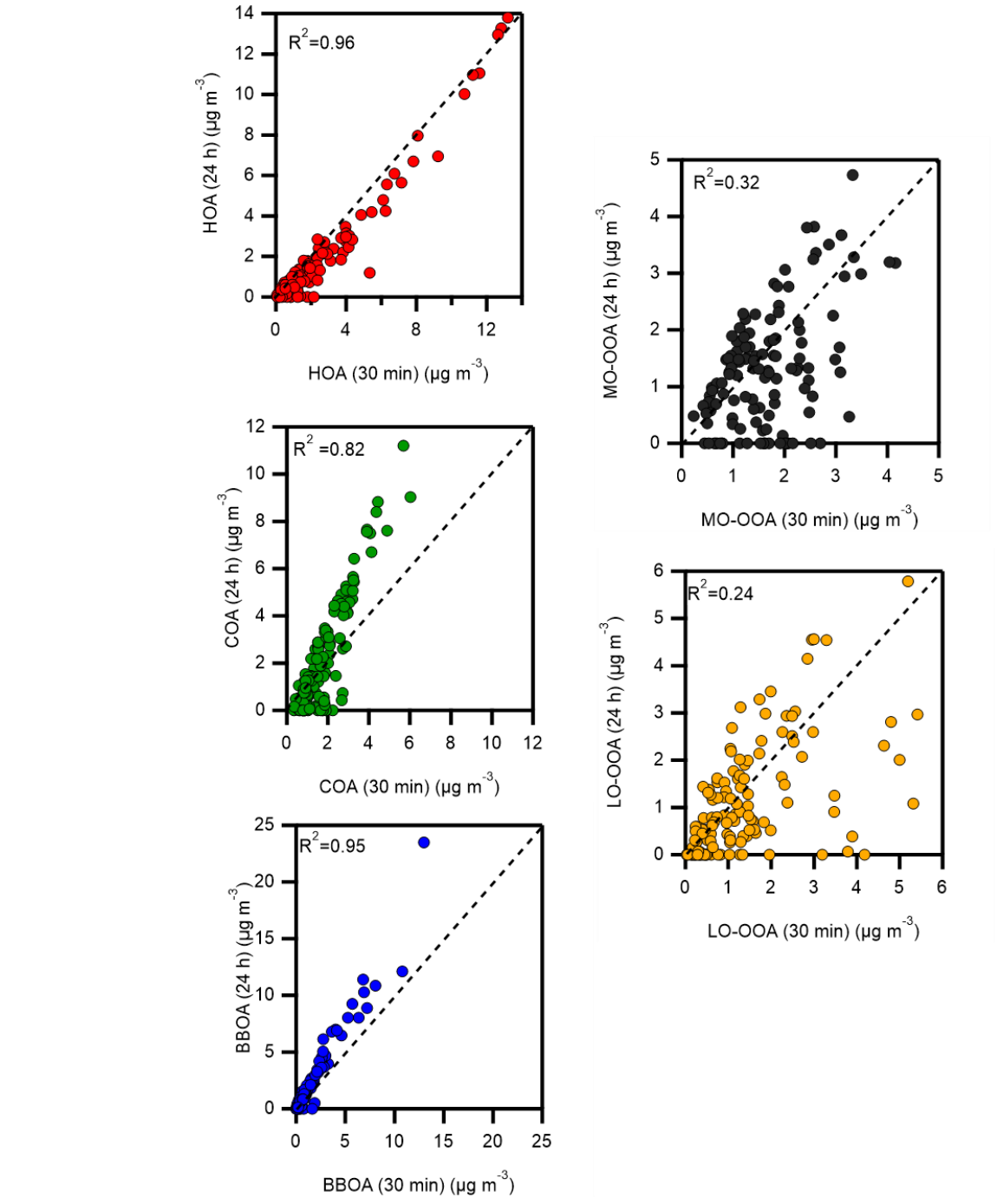


**Figure 8:** Comparison between the results of the 24 h analysis and the daily averages of the 30 min analysis for each factor for the cold period. The 1:1 lines are shown. Different axes are used.

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Preprint. Discussion started: 22 April 2022


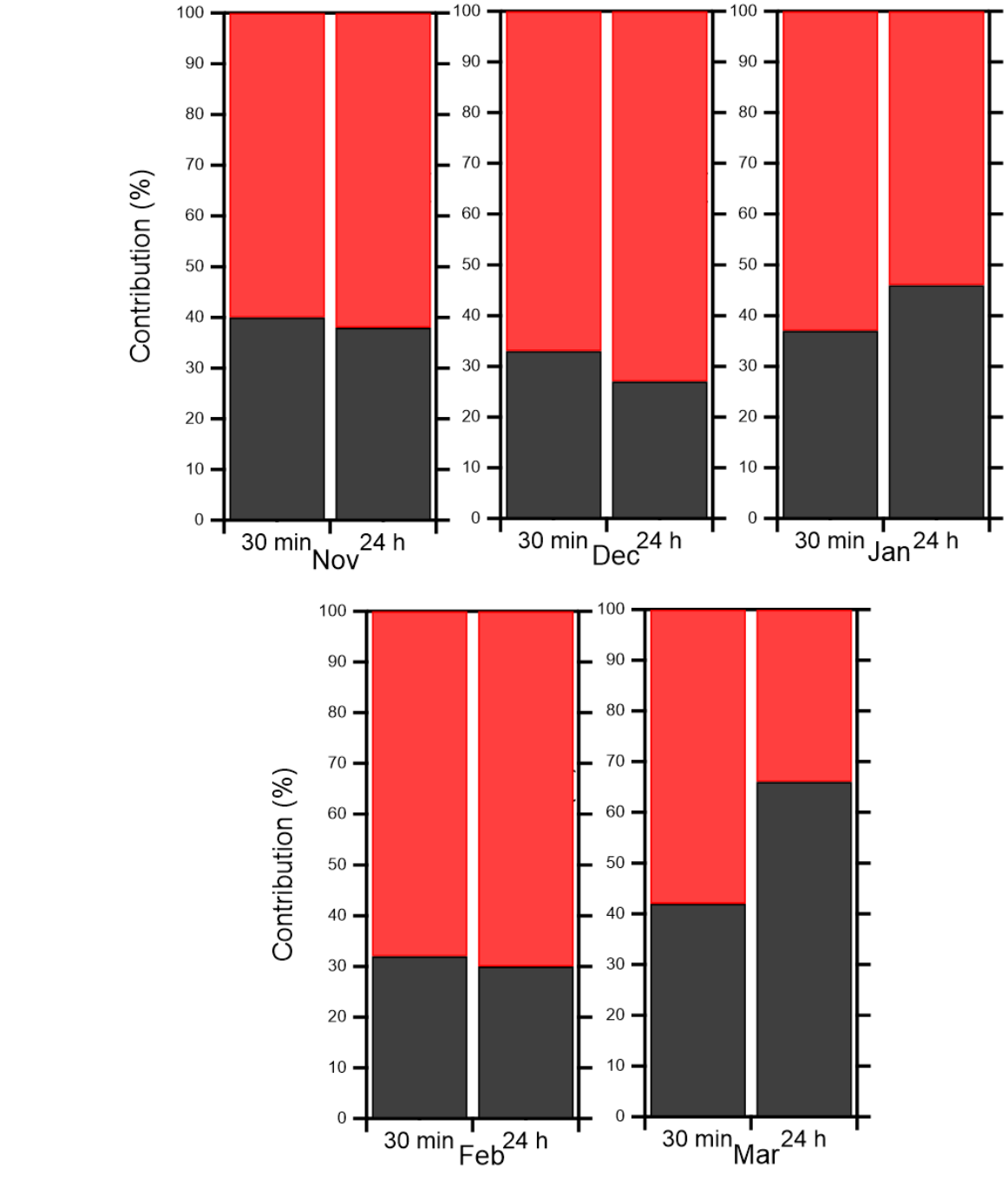


**Figure 9:** Primary (red) and secondary (black) contribution to the total OA for the high and the low time resolution results for each month.

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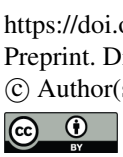
Preprint. Discussion started: 22 April 2022

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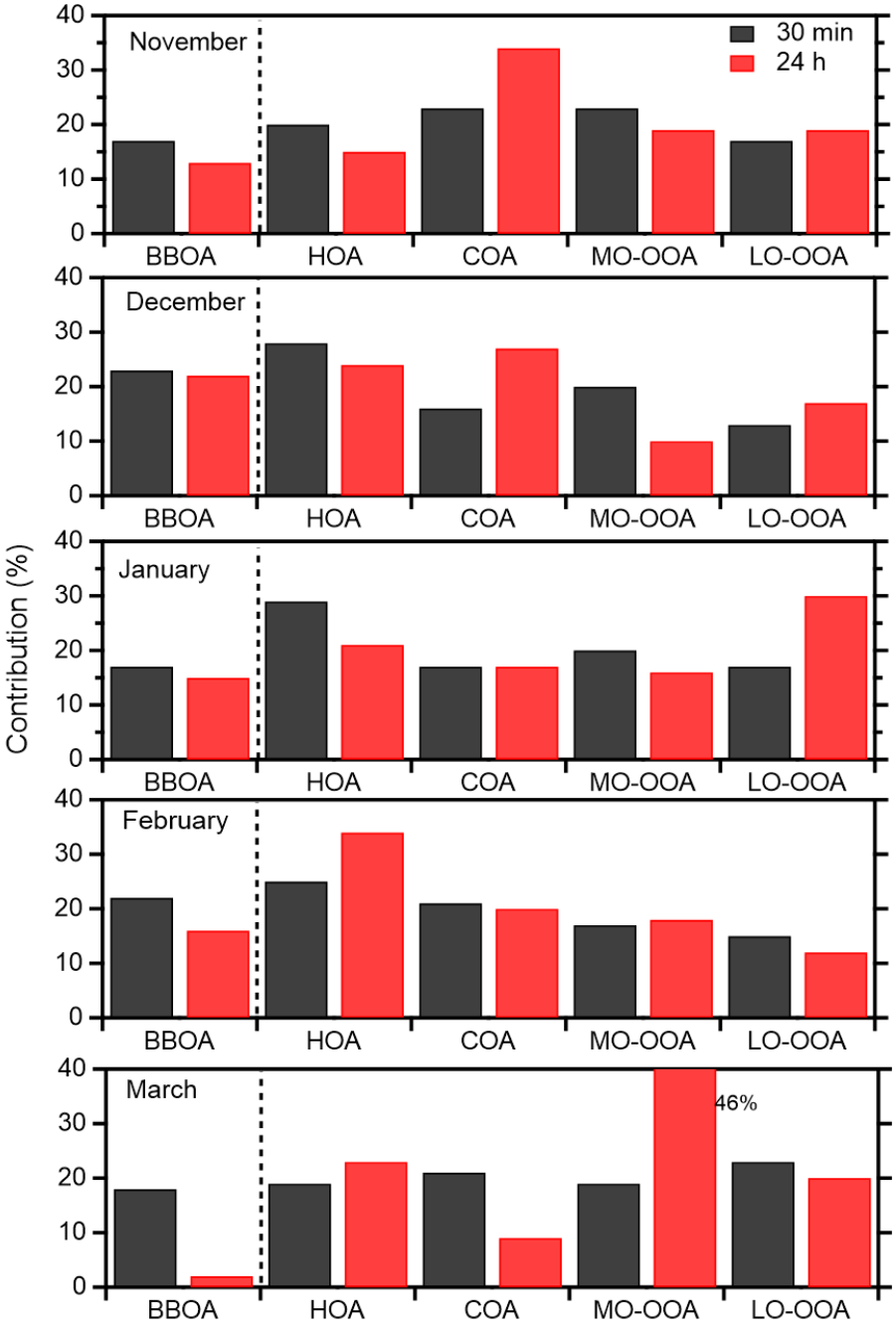


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**Figure 10:** High and low time resolution contribution of each factor to the total OA for each month individually.