

Reply to reviewers

acp-2014-970

Chemical characterization of submicron regional background aerosols in the Western Mediterranean using an Aerosol Chemical Speciation Monitor

The authors would like to thank the reviewers for their comments and suggestions, which helped improving the quality of this work. A new version of the manuscript has been prepared following the suggestions from the reviewers. We provide below detailed replies to each of the comments in a point-by-point manner.

Reviewer#1. The manuscript of Minguillón et al. represents the results obtained by using an Aerosol Chemical Speciation Monitor over a one-year period in a regional background station of the Western Mediterranean (Montseny, Spain). The mass concentrations of submicron organics, sulphate, ammonium, nitrate and chloride obtained by the ACSM are compared to concurrent off-line PM1 chemical (for inorganics) and thermal-optical (for organic carbon) analysis of filters. The sum of the ACSM components, using a time-dependent collection efficiency instead of the widely used constant 0.5, together with black carbon correlated well with PM1 concentrations determined by an optical particle counter. Nevertheless discrepancies were observed, mainly for organics, which was attributed to an underestimation of the relative ionization efficiency of the organic aerosol (OA). The importance of these discrepancies become more important if one considers the fact that the OA was found to be the major constituent of the submicron aerosol throughout the year. The source apportionment of the OA, using the ME-2 toolkit within the Positive Matrix Factorization analysis environment, revealed three major sources both during summertime and during wintertime, as well. During summer the main OA identified were hydrocarbon-like OA (HOA), and two oxygenated OA; one semi-volatile (SV-OOA) and one of low volatility (LV-OOA). During winter again an HOA was identified, together with a biomass burning OA (BBOA) and oxygenated OA (OOA), while the two different OOA components that were identified during summer could not be resolved. Finally, focusing on an intense wildfire episode close to the measurement site, a BBOA profile was identified, which was found to be very similar to BBOA profiles formerly identified in former studies at the same site, establishing a region-specific BBOA_MSY mass spectrum.

The paper is well written and easy to follow, though there are several details missing and more thorough discussion should be made in specific sections. Other than that the paper can be recommended for publication after addressing the issues listed below.

Reviewer#1. Specific comment 1) One of the main features of the manuscript that the authors draw our attention to is the comparison of the ACSM data with collocated off-line PM₁ measurements and with total PM₁ measured by an optical particle counter. Nevertheless it is clearly stated that the OPC is corrected with the simultaneous 24h gravimetric measurements, but there is no mentioning of why the gravimetric measurements are believed to be the reference. Quartz filters are known to absorb water and volatile organics, depending on the sampling protocol (preheated filters or not). I assume that, as no preheating of the filters is mentioned, there was none, but still, with the high RHs that can be seen in Figure S2, how is it guaranteed that the filters do not contain significant amounts of humidity from the sampling? Apart from the Quartz filters, are there also any Teflon filters, which are not expected to absorb neither water nor volatiles, collected in order to compare? Furthermore, I would expect a significant daily variability in the 30-min ACSM measurements that, for sure, cannot be captured in the 24h filters. Therefore, how is this correction made? Finally, in Cusack et al. (2013) it is mentioned that a Scanning Mobility Particle Sizer (SMPS) is also located in the Montseny Station; were the PM₁ concentrations (ACSM+BC) compared to the mass estimated using the SMPS volume?

Reply to Reviewer#1. Specific comment 1)

The authors acknowledge the limitations of the gravimetric determination of total PM₁, and are aware of the possible artifacts. It should be noted that the PM₁ high-volume sampler is located in a container with controlled temperature (as explained in the methods section), which reduces the negative artifacts due to volatilization of some components (mainly organic matter) at high temperatures that could occur in summer. Regarding the quartz filters treatment: the filters were pre-treated at 220°C during four hours before sampling, and filters were stabilized at controlled T and RH (20°C and 50% relative humidity) before weighing before and after sampling, according to EN12341 standard. Therefore, it is true that the filters can contain some water, not eliminated during the stabilization period, but it is expected to be a low proportion of the total mass. In any case, the authors consider that it is better to correct the OPC data with the gravimetric measurements than not correcting it at all, and they follow the guidelines for data treatment obtained from real-time PM_x determination (Alastuey et al., 2011, "PM₁₀ measurement methods and correction factors: 2009 status report", http://acm.eionet.europa.eu/docs/ETCACM_TP_2011_21_PM10Equivalence.pdf). In this report it is stated that measurements from real-time monitors should be compared with simultaneous gravimetric measurements and corrections should be applied. The correction is made as follows: real-time PM₁ concentrations from OPC are daily averaged and compared to 24-h gravimetric PM₁ concentrations. The parameters resulting from this comparison are then used to correct the hourly PM₁ data from the OPC.

The text in the revised manuscript has been modified to include the details on filter stabilization, and to include the reference where the correction of real-time measurements method is explained:

"Gravimetric PM₁ determination was carried out by weighing the filters before and after sampling, after stabilization in a conditioned room (20°C and 50% relative humidity)."

“PM₁ hourly concentrations were measured using an optical particle counter (GRIMM, model 180) and corrected with the simultaneous 24-h gravimetric measurements (Alastuey et al., 2011)”

Unfortunately, there are no Teflon filters available for the sampling period.

The PM₁ concentrations calculated from ACSMcomponents+BC were compared to the mass estimated using the SMPS volume for 2012 period (given that SMPS data were not available for 2013), resulting in a slope close to unity with a squared Pearson correlation coefficient of 0.77. This information has been added in the revised version of the manuscript in the methods and the results section. Moreover, the figure below has been added in the supplementary material as Figure S4.

Methods: “Particle number size distributions (9-820 nm) were measured by a Scanning Mobility Particle Sizer (SMPS), comprising a DMA connected to a CPC (TSI 3772), with a system designed and manufactured at the Leibniz Institute for Tropospheric Research (Wiedensohler et al., 2012). The mass concentration from SMPS data was calculated from the total volume of particles and the composition-dependent density calculated based on the ACSM chemical composition.”

Results: “The sum of ACSM components and BC concentrations was also compared to the mass concentration calculated from SMPS data, resulting in a strong correlation (squared Pearson correlation coefficient, $R^2=0.77$) and a slope very close to unity (0.997) (Figure S4).”

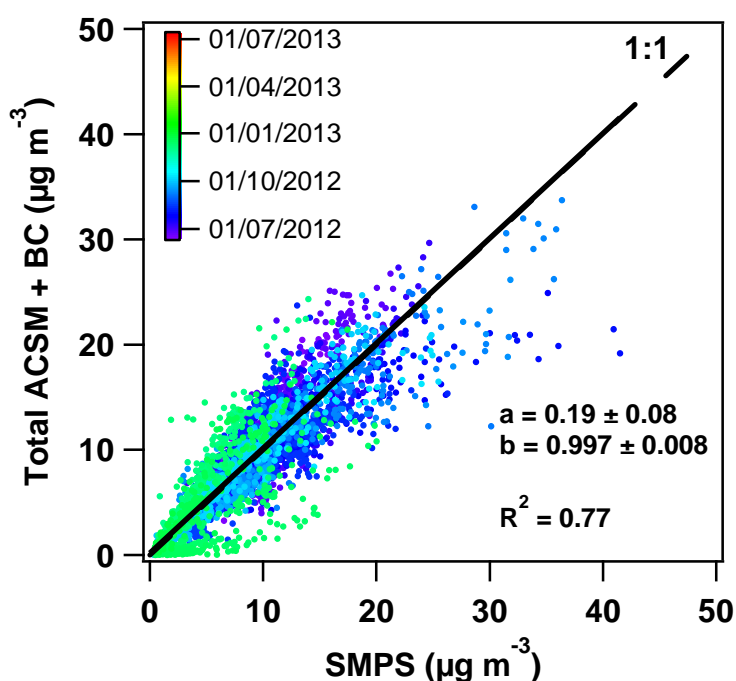


Figure S4. ACSM components + BC concentrations vs mass concentration calculated from Scanning Mobility Particle Sizer (SMPS) data coloured by the sampling time (dd/mm/aaaa). Data availability for SMPS data covered only 2012 period. Line and parameters correspond to least orthogonal distance fit ($y=a+bx$). The wild fire period is excluded from the fit.

Reviewer#1. Specific comment 2) It is mentioned in the manuscript that instead of a constant, collection efficiency (CE) of 0.5, a time-dependent CE is used, following the approach of Middlebrook et al. (2012). In the cited paper, an algorithm is developed in order to calculate composition-dependent CE values, in order to account for acidic sulfate particles, aerosol containing a high mass fraction of ammonium nitrate and high organic fraction from biomass burning emissions. In the current manuscript there is no mention of the aerosol acidity, biomass burning emissions appear to be limited and also nitrate concentrations seem to have a maximum contribution (around 20%) during winter. It would be helpful if the authors provided, even in the supplementary material, a figure that shows if and how much the used time-dependent CE deviated from the constant 0.5, especially if there is a seasonal variability observed.

Reply to Reviewer#1. Specific comment 2)

A short explanation of how much the CE differs from the default 0.45 value is included in the revised manuscript, as well as a figure with the CE time series in the supplementary material:

“The time-dependent CE equalled the default value of 0.45 for most of the period, and increased up to 0.65 during the colder period (Figure S3).”

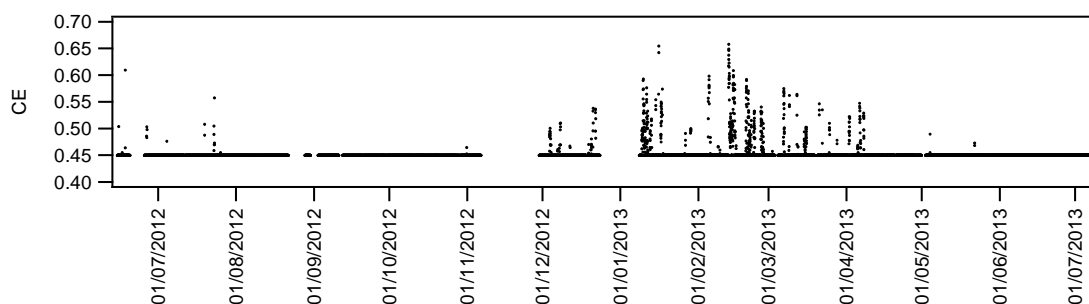


Figure S3. Time-dependent CE calculated with the Middlebrook approach (Middlebrook et al., 2012).

Reviewer#1. Specific comment 3) The claim that the second identified factor by the PMF analysis, during the wildfire episode, is and Aged BBOA, clearly needs a better reasoning and a more thorough discussion. The mass spectrum is very similar with common OOA found in the literature and no correlations are given with external tracers, such as black carbon, to support this assumption. Furthermore, why should that OOA factor have only one source origin and not be, partially, a pre-existing, background OOA that, clearly from the time series, may be also the end product of atmospheric transformation of BBOA, as well? What do their diurnal variability look like, is it similar? My greatest concern is the nomenclature, solely stating it as “Aged BBOA”.

Reply to Reviewer#1. Specific comment 3)

The main goal of the source apportionment of OA carried out for the period of this event was to clearly differentiate the fresh BBOA contribution, from aged or background OA. Hence, different tests were carried out until reaching a satisfactory solution with two factors, one of them clearly identified as BBOA. Given the high impact of the wildfire event on the ambient

submicron aerosol concentrations, the authors made the assumption that the rest of the contributors to ambient concentrations during the wildfire event were close to negligible. This fact, together with the time series of the second OA factor identified for this episode (tracking partially that of BBOA factor), led the authors to name this factor as Aged BBOA. Nevertheless, the authors agree that the source profile resembles that of typical OOA factors and that a contribution from other OOA may also take place during the episode. Therefore, the name of the factor has been changed to simply OOAm (where the m stands for mix). The discussion on the wildfire event has been modified accordingly as follows:

“In order to investigate the wildfire source, an unconstrained source apportionment (PMF) of the organic aerosol fraction during this episode was carried out. The PMF resulted in two factors, one representing the fresh biomass burning organic aerosol (named as BBOA_MSY) and another one interpreted as the mix of other OA sources and aged BBOA, named as OOAm (where the m stands for mix). The interpretation of the factors is based on their mass spectral source profiles and the time series of their contributions. The BBOA_MSY shows higher peaks for the specific tracers of biomass burning (m/z 60 and m/z 73) (Alfarra et al., 2007) than the OOAm, which indicates that the primary BBOA is well represented by this factor. Moreover, the f_{44} (ratio of m/z 44 (mostly CO_2^+) to total signal in the component mass spectra), an indicator of oxygenated organic species (Alfarra et al., 2007), was higher for the OOAm than for the BBOA_MSY factor, which indicates that this factor corresponds to a more oxidized aerosol. On the other hand, the f_{43} is higher than the f_{44} in the BBOA_MSY factor, whereas it is the other way around (f_{44} much higher than f_{43}) in the OOAm. These differences in relative intensities indicate the differences in the age of the aerosol (Ng et al., 2010) and further lead to differentiate the factors as fresh BBOA and OOAm. The SOA formation from biomass burning has been reported to be quick (Heringa et al., 2011), and hence part of the OOAm factor is formed of aged BBOA, which also explains that the time series of the OOAm factor partially tracks that of the BBOA_MSY. The BBOA_MSY profile found here is very similar to a BBOA profile found for Montseny in March 2009 (Minguillón et al., 2011) (<https://sites.google.com/site/amsglobaldatabase>) and to an average profile for BBOA from various datasets (Ng et al., 2011a) (Figure S9). The f_{60} in the BBOA_MSY factor is 0.014, similar to the f_{60} in these other two BBOA profiles (0.017 and 0.024). It has been also compared to the BBOA found in the background of Paris (Crippa et al., 2013), with which some more differences were found, mainly our profile has higher m/z 43 and m/z 41 signals and lower m/z 60 (Figure S9). This BBOA_MSY mass spectrum is considered specific for the study area and hence it can be later used for other studies in the region, to be fed to the ME-2 model in order to quantify the BBOA contribution. We have done so in the present study for the winter period. Whereas the time series of both factors were similar, the BBOA_MSY contribution showed more intense peaks, and the increase in the OOAm was slightly higher for the second part of the main peak on the 23 July.”

Reviewer#1. Specific comment 4) I would have expected, even in the supplementary material, a more thorough discussion on the selected PMF solutions; stability of the solution, residuals, correlations with external tracers, possibly a more detailed comparison with external mass spectra (e.g. squared Pearson coefficients).

Reply to Reviewer#1. Specific comment 4)

The variation of atmospheric aerosols in the regional background is usually driven by the transport of pollutants from nearby polluted areas, with little influence from local sources, and some influence from local atmospheric processes. Montseny site is not an exception and therefore several aerosol components show the same variation. For instance, whereas the diurnal variation of HOA in a city is usually characterized by the two rush hour peaks and nicely correlates with BC, the HOA found at Montseny is the result of the transport from the polluted areas, and therefore the diurnal pattern is characterized by a single increase around midday, as it happens with the rest of pollutants. This is a drawback to use the correlations among different pollutants with the aim of confirming their common origin. This is the case for the different organic sources found at Montseny. Nevertheless, the authors did study the correlations between the OA sources time series with external tracers, but results were interpreted with caution bearing in mind the characteristics described above. This is the reason for not giving too much relevance to these correlations in the manuscript. However the authors understand the need for a more thorough discussion of the selected PMF solutions and it has been included in the revised manuscript, as well as an additional figure in the supplementary material.

The text in the revised manuscript is now as follows:

“The application of ME-2 to the warmer period resulted in a solution with 3 factors: a hydrocarbon-like OA (HOA), a semi-volatile oxygenated OA (SV-OOA) and a low-volatile oxygenated OA (LV-OOA). This solution was chosen based on several tests with different number of factors and different α -values for the constrained factors, taking into account the correlations with external data, the diurnal patterns and the residuals, following the strategy described by Crippa et al. (2014) and Canonaco et al. (2013). The HOA factor was constrained using an average HOA factor (HOA_avg) from different datasets (Ng et al., 2011a). An α -value range from 0.05 to 0.3 was explored and an α -value of 0.2 was finally selected, which was a compromise between a higher Squared Pearson correlation coefficient between HOA and BC (which increased when increasing the α -value) and the physically meaningful profiles of the whole solution (i.e. assessing the profiles of the LV-OOA and SV-OOA factors). BC concentrations correlated moderately with HOA (squared Pearson coefficient $R^2 = 0.51$). The SV-OOA shows higher 43-to-44 ratio compared to the LV-OOA, together with a lower f44, which are the main differences between these two profiles (Figure 8a). The BBOA contribution in summer is expected to be low based on previous studies carried out in July 2009 (Minguillón et al., 2011) and on the low f60 registered in the present study in summer (Figure S10), which is below the background threshold (0.003) established by Cubison et al. (2011). Hence, the BBOA factor was not identified and it was not constrained by the ME-2 in summer.

During the warmer period, the HOA accounted for 13% ($0.7 \mu\text{g m}^{-3}$), whereas the LV-OOA and the SV-OOA accounted for 45% and 42% of the total OA ($2.4 \mu\text{g m}^{-3}$ and $2.2 \mu\text{g m}^{-3}$), respectively (Figure 8c). As explained before, the location and meteorological conditions at MSY result in an increase of pollutants concentrations starting at mid-morning, caused by the breeze transport from populated areas to the regional site. This variation is clearly observed for BC (Figure 9), which showed a moderate correlation with HOA ($R^2 = 0.51$). Nevertheless, the

midday increase in the concentration of SV-OOA is larger than that of BC, and therefore it cannot be only explained by the transport of pollutants, including the SOA formed during the transport, but it is attributed to the formation of SOA during these hours in MSY. Hence, the SOA formation can be estimated as the additional increase with respect to that of BC (considered in % of the average concentration during the night hours), which results in a local SOA formation of $1.1 \mu\text{g m}^{-3}$. This SOA may result mainly from biogenic precursors, in agreement with the 70% of non-fossil SOA found in March 2009 (Minguillón et al., 2011). The flatter diurnal pattern of LV-OOA (Figure 9) points to a more regional and well-oxidized aerosol, which could be interpreted as the regional background SOA. This SOA formation during warm periods was also observed by Cusack et al. (2013), who studied nucleation and particle growth events, identifying both of them even under polluted conditions at MSY.

In the colder period, the application of ME-2 resulted in a solution with 3 factors: hydrocarbon-like OA (HOA), biomass burning OA (BBOA) and oxygenated OA (OOA) (Figure 8b). A solution with two OOA factors was investigated and it was not meaningfully interpretable. Probably the small temperature range variation in winter results in not enough diurnal variation in f43 and f44 for a split of the OOA in SV-OOA and LV-OOA. As per the warmer period, the final solution was chosen based on the strategy described by Crippa et al. (2014) and Canonaco et al. (2013). The residuals for the chosen solution did not show any daily pattern or m/z -dependent pattern, which is a good indicator that the selected solution explains the OA variation. For coherence with the warmer period, the HOA factor was based in an average HOA factor (HOA_avg) from different datasets (Ng et al., 2011a), and it was constrained with an a -value of 0.1. This a -value was chosen based on the correlation between the HOA contribution and the BC concentrations found for different a -values tests. The HOA contribution shows a relatively strong correlation with BC concentrations (squared Pearson coefficient $R^2=0.70$). The HOA spectral profiles found for summer and winter are quite similar, and hence the HOA contributions in summer and winter can be compared directly. The BBOA factor was decided to be constrained based on the f60 signal, which was above the aforementioned threshold of 0.003 (Figure S10). It was based in the BBOA_MSJ profile found for the wildfire episode that took place during this study, constrained with an a -value of 0.1. The a -value was chosen with the following criteria: preference for a low a -value given that the anchor profile used was site-specific, residuals for the m/z 60 not showing any diurnal pattern, contribution of the BBOA factor to the total m/z 60 (which reached 64% for the chosen solution). The resulting BBOA profile has a higher m/z 44 signal than the BBOA_MSJ, which may indicate differences in the biomass burning emissions from the wildfire event compared to the emissions from regular biomass burning, or it could indicate that the BBOA contribution identified here may be partially mixed with some oxidized OA. The single winter OOA factor identified shows higher f44 than both LV-OOA and SV-OOA in summer. This higher degree of oxidation of the OA in winter indicates that there is less newly-formed SOA during winter compared to summer. A similar variation was observed in Zurich (Canonaco et al., 2014). The OOA contribution correlates moderately with sulphate ($R^2=0.49$), relatively strongly with nitrate ($R^2=0.73$) and more strongly with ammonium ($R^2=0.79$).

The major OA constituent in winter was the OOA, with 59% ($1.5 \mu\text{g m}^{-3}$), whereas the HOA and BBOA accounted for 12% ($0.3 \mu\text{g m}^{-3}$) and 29% ($0.7 \mu\text{g m}^{-3}$) of the total OA, respectively (Figure 8d). Note that the BBOA contribution may be mixed with some OOA as stated before, given

the relatively high signal at m/z 44 and hence the pure BBOA contribution would be lower than that determined. Actually it accounts for 6% of the total signal at m/z 44. Nevertheless, strong correlation ($R^2=0.77$) was found between the BBOA contribution and the potassium concentrations determined in 24-h PM_{10} samples (Figure S11), which further confirms the existence of this source at MSY in winter. The relative BBOA contributions found in the present study are similar to those found in a previous study in March 2009 using a HR-ToF-AMS, where the HOA represented 7% of the total OA, the BBOA contributed with 9% and the rest was attributed to OOA (Minguillón et al., 2011; Crippa et al., 2014). The discrepancy in the BBOA contribution (29% vs 9%) may be due to the different sampling periods (the current study included Nov 2012-March 2013 whereas the previous study only included March 2009), to the mixture of some OOA in the BBOA factor for the present study, and/or to the possible increase of biomass burning due to the climate and energy policies in the last five years.

The average daily pattern shown by the different OA sources in winter (Figure 9) resembles that of BC, nitrate, sulphate and ammonium (Figure 5), with an increase of pollutants concentrations starting at around 10h UTC and reaching high concentrations at around 13h UTC. This daily increase is attributed to the transport from populated areas to the mountain site with the breeze. This variation is observed for all the components and therefore the local formation of SOA is deduced to be low in winter.”

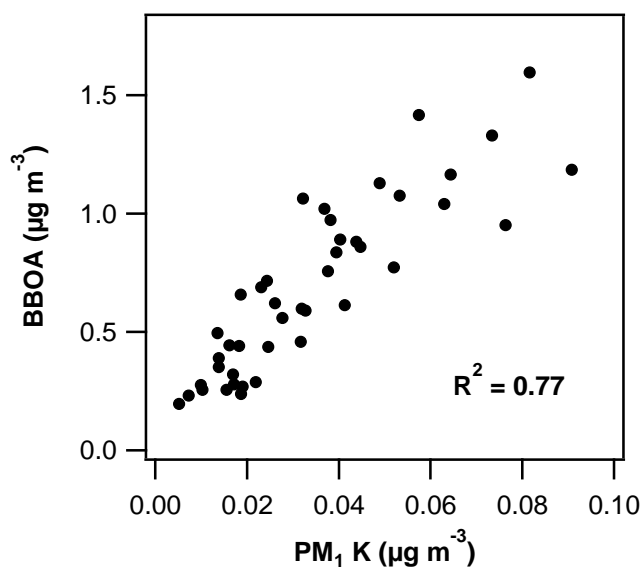


Figure S11. Contribution of BBOA in winter (averaged to 24-h periods matching the filter sampling) vs potassium concentrations in PM_{10} .

Reviewer#1. Technical correction 1) P967, L6: Carbonaceous aerosols are comprised of...

Reply to Reviewer#1. Technical correction 1)

It has been corrected.

Reviewer#1. Technical correction 2) P968, L21: ...was estimated to be (instead of “estimated in”)

Reply to Reviewer#1. Technical correction 2)

It has been corrected.

Reviewer#1. Technical correction 3) P970, L2: ...the Azores, highly favors... (instead of “high”)

Reply to Reviewer#1. Technical correction 3)

The authors meant that the entry of clean Atlantic air masses is favoured by the Azores high. To avoid confusion, the text has been edited as follows: “...the location of the Azores high pressure system favours the entry of clean Atlantic air masses...”

Reviewer#1. Technical correction 4) P975, L5: It is not clear whether the comparisons are made before or after the ACSM components concentrations are calculated using the time-dependent collection efficiency or from the raw data. Because, how can it be that slope between the sum of the ACSM+BC is very close to unity compared to the PM₁ concentrations from the OPC (which is corrected with the 24h gravimetric measurements) but ammonium from the ACSM is almost double, nitrate is 2.8 times higher and organic matter is 4.25 times higher than the OC from the filters?

Reply to Reviewer#1. Technical correction 4)

The comparison of the concentrations of the ACSM components with the concentrations measured on filters was made after applying the time-dependent collection efficiency. The apparent discrepancy between the slopes obtained for ACSM+BC vs PM₁ from OPC (corrected with gravimetric measurements) and the slopes for the different components is attributed to the undetermined fraction of PM₁ mass in the filters. Thus, whereas the ACSM+BC concentrations are strictly the sum of the components, the PM₁ concentrations include a fraction of undetermined mass, partially attributed to water. The following clarification has been added to the main text in the revised manuscript together with a figure illustrating this explanation in the supplementary material:

“The apparent discrepancy between the slope for total PM₁ (ACSM+BC vs PM₁ from OPC corrected with gravimetric measurements, close to unity) and the slopes for the different components (>1) is attributed to the undetermined fraction of PM₁ mass in the filters. Thus, whereas the ACSM+BC concentrations are strictly the sum of the components, the PM₁ gravimetric concentrations include a fraction of undetermined mass, partially attributed to water (Figure S5).”

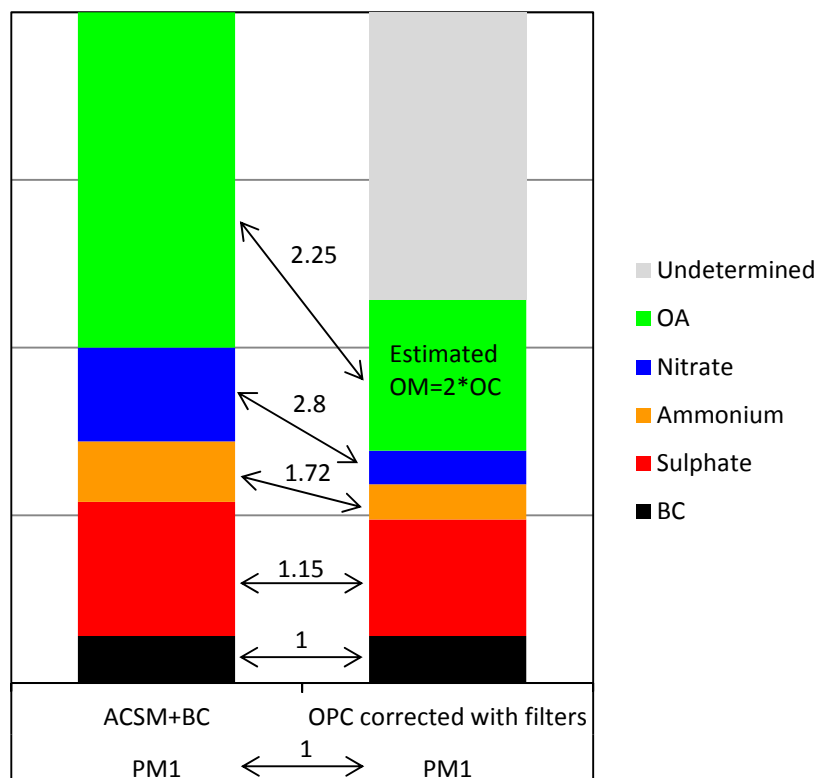


Figure S5. Schematic comparison of ACSM components + BC concentrations vs PM_1 concentrations from OPC corrected with gravimetric determinations. The numbers indicate the slopes found for experimental data for Montseny during June 2012 to July 2013. The 2.25 corresponds to the slope of OA (ACSM) vs OM estimated from OC (filters) as $2 \cdot OC$.

Reviewer#1. Technical correction 5) P975, L12: It is stated that the slopes of sulphate and ammonium are relatively close to unity. For sulphate this may be the case (1.15) but for ammonium, I wouldn't call 1.72 close to unity, as it is closer to be the double.

Reply to Reviewer#1. Technical correction 5)

The text related to the discussion of the slopes has been changed as follows:

“For the strongly-correlated species, the slopes (ACSM vs off-line measurements) were different for each of them. Whereas it was close to unity for sulphate (1.15), it was higher for ammonium (1.72), and much higher for nitrate (2.80). The final reasons for this discrepancy remain unexplained, although a possible cause is the volatilization of ammonium nitrate from the filters.”

Reviewer#1. Technical correction 6) P975, L20-25: Based on Aiken et al. (Environ. Sci. Technol. 42, 4478-4485, 2008) an estimate is proposed in order to calculate the OM-to-OC ratio base on the f44. Was this estimate used in order to see whether it compares to the slope obtained? Even though indeed, SOA is expected to have a high contribution at Montseny, I wouldn't expect a conversion factor for OC to OM higher than 2.2-2.4.

Reply to Reviewer#1. Technical correction 6)

The calculation of OM-to-OC ratio from the f44 based on Aiken et al. (2008) is not suitable for ACSM instruments, as recently learnt from an intercomparison of 13 Q-ACSM instruments (Fröhlich et al., 2015, Atmos. Meas. Tech. Discuss. 8, 1559-1613). During this intercomparison exercise, different f44 values were recorded by the different ACSM instruments, although they all followed the same trend. Therefore, the study concluded that in absence of specific calibration with organic standards, the calculation of O:C values (and OM:OC) from the f44 should be done with caution. Consequently the authors decided not to calculate the OM-to-OC ratios from the f44 in the present study. It should be noted that the intercomparison study also concluded that the precision of an individual, stable instrument is good and relative changes observed can be unambiguously interpreted, and that the source apportionment analyses are not compromised, and the influence on the mass contributions of the organic sources calculated with ME2 are minor. To include such clarifications, the following text has been added in the end of section 3.1 in the revised manuscript:

“The calculation of OM-to-OC ratio from the f44 based on Aiken et al. (2008) was not carried out given that it is not suitable for ACSM instruments, as recently learnt from an intercomparison of 13 Q-ACSM instruments (Fröhlich et al., 2015)”

It is true that the 4.25 ratio is very high, even for pure SOA, and it is higher than the OM-to-OC ratio determined for Montseny in March 2009 (Minguillón et al., 2011, Atmos. Chem. Phys. 11, 12067-12084). That is why two possible hypothesis about why we obtain this high ratio are discussed in the manuscript. The discussion in the revised manuscript has been modified to include the OM-to-OC ratio determined for Montseny in March 2009:

“This large OM-to-OC ratio suggests photochemically well-aged organics, but it is too high even for a pure SOA (Aiken et al., 2008), which is expected to have an important contribution at MSY as will be discussed later (section 3.5), and it is higher than the OM-to-OC ratio determined in March 2009 at Montseny (2.0) (Minguillón et al., 2011). This extremely large OM-to-OC ratio might be attributed to...”

Reviewer#1. Technical correction 7) P977, L20: ...due to shipping emissions (delete “the”)

Reply to Reviewer#1. Technical correction 7)

It has been corrected.

Reviewer#1. Technical correction 8) P981, L15-16: Apart from the MAAP, is there an aethalometer available at Montseny station, in order to get and estimate on BC source apportionment? I would expect correlations with BC from fossil fuel and/or BC from wood burning to be higher.

Reply to Reviewer#1. Technical correction 8)

There are in fact aethalometer data available for this period at Montseny, but the dataset has not been assessed and interpreted thoroughly yet, as it will be the focus of future publications. Nevertheless, a preliminary data treatment is available and the BC_{ff} (BC from fossil fuel) and BC_{wb} (BC from wood burning) have been estimated (Marco Pandolfi, from IDAEA-CSIC, is acknowledged for this). The results are encouraging, in the sense that the BC_{wb} time series shows a meaningful seasonality, with higher values during the colder period. However, the BC due to biomass burning contributions at Montseny is very low on average, and hence the aethalometer method to separate this BC_{ff} and BC_{wb} may not work as accurately as for areas with high biomass burning influence, such as the Alpine areas, from where the dataset was used to develop the method (Sandradewi et al., 2008, Environ. Sci. Technol. 42, 3316-3323). The authors did test the correlations of the preliminary estimated BC_{ff} with HOA, but the resulting correlation coefficients were similar or even worse than those for total BC. For example, for the warmer period, to which the reviewer makes reference to in the present comment, the HOA vs BC squared Pearson coefficient was 0.51, and the HOA vs BC_{ff} squared Pearson coefficient was 0.44. Consequently, given the fact that the aethalometer results are still preliminary, the authors decided not to include such information in the present paper.

Reviewer#1. Technical correction 9) Figure S6: What is the difference between the two diagrams in the bottom? Because all axes and annotations are the same. From what I gather, the panel in the left seems to be the so-called Aged BBOA and not the BBOA.

Reply to Reviewer#1. Technical correction 9)

The figure in the right meant to be a zoom from figure in the left, with the scale from 0.00 to 0.03, in order to show better the m/z with low contributions to the factor, mainly the m/z 60, with high relevance for the biomass burning profile. It has been now explained in the figure caption as follows:

“Figure S9. Comparison of the BBOA factor found for the wildfire episode (BBOA_MSY) with other BBOA profiles found in the literature (Minguillón et al., 2011;Ng et al., 2011;Crippa et al., 2013). The scatter plot on the right is a zoom for values from 0.00 to 0.03.”

Reviewer#2. In this manuscript, the authors report on 2-month field campaign deploying an ACSM and MAAP and describe their measurements against mass, organic carbon, and elemental composition obtained with collocated PM1 filter measurements. After describing the choices for constrained and unconstrained parameters, the results of the ACSM with respect to organic aerosol fraction, speciation, and sources for the region are discussed. The authors synthesize a large quantity of information and present new and interesting evaluations for the ACSM. The basis of the work is of sound quality and the topic is relevant for readers of Atmospheric Chemistry and Physics, and is therefore recommended for publication. There are several points which are recommended for consideration before publication.

Reviewer#2. General comment 1) Can the RIE and CE be assessed independently of one another? In the case of external mixing, the acidity-corrected CE may not apply to that of organics (as reported by Hawkins and Russell, 2010), and quartz fiber filters are known to have adsorption artifacts (though this would not help the argument of extremely high OA/OC ratio).

Hawkins, L. N., L. M. Russell, D. S. Covert, P. K. Quinn, and T. S. Bates. "Carboxylic Acids, Sulfates, and Organosulfates in Processed Continental Organic Aerosol over the Southeast Pacific Ocean during VOCALS-REx 2008." *Journal of Geophysical Research* 115, no. D13 (July 2, 2010). doi:10.1029/2009JD013276.

Reply to Reviewer#2. General comment 1)

The CE was applied to the total mass spectra and therefore it affected equally all the components of the atmospheric aerosol. This was done according to the agreement within the European ACTRIS-ACSM community (<http://www.actris.net>) to apply the CE to the whole mass spectra preferably using the Middlebrook approach (<http://www.psi.ch/acsm-stations/acsm-best-practice>). Nevertheless, the authors are aware that the Middlebrook approach only works if the particles are internally mixed. At Montseny, a regional background site, it is reasonable to assume that the particles are internally mixed, and hence the application of a unique CE would be suitable. This assumption has been explained in section 2.2 (ACSM settings, calibrations and data processing) in the revised manuscript as follows:

"The aerosols at MSY are assumed to be internally mixed and thus the CE was assumed to be the same for different components in contrast to e.g. Hawkins et al. (2010)."

Reviewer#2. General comment 2) Is the ACSM PM₁ + BC expected to match the PM₁ so well (slope ~1)? I.e., was there indication of the level of mineral dust in the PM₁ samples with the ICP-MS?

Reply to Reviewer#2. General comment 2)

From the ICP analyses carried out with the PM₁ filter samples, the mineral matter in PM₁ was below 0.3 $\mu\text{g m}^{-3}$ for all the sampling period except for eleven specific days with a strong influence of Saharan dust, which affected also the PM₁ fraction. For six of these days, the mineral matter concentration ranged from 0.3 $\mu\text{g m}^{-3}$ to 1 $\mu\text{g m}^{-3}$, and only for the remaining five days the mineral matter concentration ranged from 1 $\mu\text{g m}^{-3}$ to 2 $\mu\text{g m}^{-3}$. Likewise, the sea spray contribution was below the detection limit of 0.25 $\mu\text{g m}^{-3}$. Therefore, there are no major contributors to PM₁ mass other than the ACSM components and the BC for the sampling period at Montseny.

Reviewer#2. General comment 3) An approximate OM/OC ratio for ACSM alone can be calculated independently of the filter OC based on the parameterization of Aiken et al. (2008) assuming the same instrument response; it may be worth discussing ACSM OC vs. filter OC or ACSM OA vs. filter OA to focus the problem on the sampling artifacts.

Reply to Reviewer#2. General comment 3)

The calculation of OM-to-OC ratio from the f44 based on Aiken et al. (2008) is not suitable for ACSM instruments, as recently learnt from an intercomparison of 13 Q-ACSM instruments (Fröhlich et al., 2015, Atmos. Meas. Tech. Discuss. 8, 1559-1613). During this intercomparison exercise, different f44 values were recorded by the different ACSM instruments, although they all followed the same trend. Therefore, the study concluded that in absence of specific calibration with organic standards, the calculation of O:C values (and OM:OC) from the f44 should be done with caution. Consequently the authors decided not to calculate the OM-to-OC ratios from the f44 in the present study. It should be noted that the intercomparison study also concluded that the precision of an individual, stable instrument is good and relative changes observed can be unambiguously interpreted, and that the source apportionment analyses are not compromised, and the influence on the mass contributions of the organic sources calculated with ME2 are minor. To include such clarifications, the following text has been added in the end of section 3.1 in the revised manuscript:

“The calculation of OM-to-OC ratio from the f44 based on Aiken et al. (2008) was not carried out given that it is not suitable for ACSM instruments, as recently learnt from an intercomparison of 13 Q-ACSM instruments (Fröhlich et al., 2015)”

Reviewer#2. General comment 4) As pointed out in Canonaco et al. (2013) and others, the apportionment of HOA, OOA, BBOA, etc. may be sensitive to the constraints imposed by the matrix decomposition. As pointed out by reviewer #1, it would be relevant to discuss the ME-2 solutions and potential uncertainties in the reported values, or discuss ranges which have been reported in the literature such that it is clear which conclusions are robust and which are subject to the assumptions of the decomposition.

Reply to Reviewer#2. General comment 4)

The discussion on the chosen PMF solution has been extended. Please refer to the Reply to Reviewer#1. Specific comment 4) for an explanation and the text included in the revised manuscript.

Reviewer#2. Minor comment 1) The authors do not mention the f60 ratios of the BBOA factors of the wildfire period.

Reply to Reviewer#2. Minor comment 1)

The discussion on the wildfire event has been changed and it directly states now the f60 values of the different BBOA profiles. The part of the text making reference to f60 reads as follows:

“The BBOA_MSY profile found here is very similar to a BBOA profile found for Montseny in March 2009 (Minguillón et al., 2011) (<https://sites.google.com/site/amsglobaldatabase>) and to an average profile for BBOA from various datasets (Ng et al., 2011a) (Figure S9). The f60 in the BBOA_MSY factor is 0.014, similar to the f60 in these other two BBOA profiles (0.017 and 0.024). It has been also compared to the BBOA found in the background of Paris (Crippa et al., 2013), with which some more differences were found, mainly our profile has higher m/z 43 and m/z 41 signals and lower m/z 60 (Figure S9).”

Reviewer#2. Minor comment 2) Figure 2. The authors may wish to write the equation $y = a + bx$ in the caption such that parameters "a" and "b" in the panels can be interpreted as intercept and slope.

Reply to Reviewer#2. Minor comment 2)

The equation has been included in the figure caption.