



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

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**Abstract.** An Aerosol Chemical Speciation Monitor (ACSM, Aerodyne Research Inc.) was deployed at the Montseny (MSY; 41°46'46" N, 02°21'29" E, 720 m a.s.l.) regional background site in the western Mediterranean, Spain, from June 2012 to July 2013 to measure real-time inorganic (nitrate, sulfate, ammonium and chloride) and organic submicron aerosol concentrations. Co-located measurements, including real-time submicron particulate matter (PM<sub>1</sub>) and black carbon (BC) concentrations, and off-line PM<sub>1</sub> chemical analysis were also carried out. This is one of the few studies that compare ACSM data with off-line PM<sub>1</sub> measurements, avoiding the tail of the coarse mode included in the PM<sub>2.5</sub> fraction. The ACSM + BC concentrations agreed with the PM<sub>1</sub> measurements, and a strong correlation was found between the concentrations of ACSM species and the off-line measurements, although some discrepancies remain unexplained. Results point to a current underestimation of the relative ionization efficiency (RIE) established for organic aerosol (OA), which should be revised in the future. The OA was the major component of submicron aerosol (53 % of PM<sub>1</sub>), with a higher contribution in summer (58 % of PM<sub>1</sub>) than in winter (45 % of PM<sub>1</sub>). Source apportionment of OA was carried out by applying positive matrix factorization (PMF), using the multilinear engine (ME-2) to the organic mass spectral data matrix. Three sources were identified in summer: hydrocarbon-like OA (HOA), low-volatile oxygenated OA (LV-OOA), and semi-volatile oxygenated OA (SV-OOA). The secondary OA (SOA; 4.8 μg m<sup>-3</sup>, sum of LV-OOA and SV-OOA) accounted for 85 % of the total

OA, and its formation during daytime (mainly SV-OOA) was estimated to be 1.1 μg m<sup>-3</sup>. In winter, HOA was also identified (12 % of OA), a contribution from biomass burning OA (BBOA) was included and it was not possible to differentiate between two different SOA factors, but a single oxygenated OA (OOA) factor was resolved. The OOA contribution represented 60 % of the total OA, with a degree of oxidation higher than both OOA summer factors. An intense wildfire episode was studied, obtaining a region-specific BBOA profile.

## 1 Introduction

Ambient aerosols have adverse effects on human health (Pope III and Dockery, 2006) and affect climate (IPCC, 2013), ecosystems, crops and regional visibility. Fine particulate matter (PM<sub>1</sub>, particles with an aerodynamic diameter < 1 μm) contains substantial fractions of inorganic compounds and carbonaceous aerosols, the latter contributing up to 90 % of the mass (Jimenez et al., 2009). Carbonaceous aerosols are comprised of organic compounds, collectively referred to as organic aerosol (OA), elemental carbon (EC) and carbonates (from mineral dust), although the latter can be considered negligible in submicron aerosols.

The western Mediterranean basin (WMB) has special atmospheric and geographic characteristics that prompt an interest in the detailed study of the ambient aerosols in this area (Querol et al., 2009). The regional background has been

investigated through long data series of measurements in previous studies from Montseny, Spain (representative of the regional background in the WMB). Pérez et al. (2008) found average particulate matter concentrations at Montseny of 17, 13 and  $11 \mu\text{g m}^{-3}$  of  $\text{PM}_{10}$ ,  $\text{PM}_{2.5}$  and  $\text{PM}_1$ , respectively, in the 2002–2007 period. Cusack et al. (2012) and Querol et al. (2014) found a decreasing trend in  $\text{PM}_{2.5}$  concentrations from 2001 to 2012 of  $-0.39 \mu\text{g m}^{-3}$  per year.  $\text{PM}_{2.5}$  concentrations were found to be higher in the WMB than at other rural background sites across Spain, Portugal, Germany and Scandinavia but lower than those measured in Switzerland, Italy and Austria (Cusack et al., 2012). The prevailing daily evolution is driven by the breeze circulation (mountain and sea breezes), with lower  $\text{PM}_x$  concentrations at night owing to the nocturnal drainage flows and higher  $\text{PM}_x$  concentrations at midday owing to the upward transport by the breeze of atmospheric pollutants accumulated in the pre-coastal depression (Pérez et al., 2008). Maximum  $\text{PM}_{10}$  concentrations were found in summer, February–March and November, and sporadic  $\text{PM}_x$  increases may be recorded under anticyclonic conditions (Pey et al., 2010). The chemical composition of  $\text{PM}_{2.5}$  is characterized by high concentrations of organic aerosol and sulfate, followed by crustal material, nitrate and ammonia, with sea spray and elemental carbon being a minor part of the total  $\text{PM}_{2.5}$  mass (Cusack et al., 2012). Compared to other central European sites, the western Mediterranean aerosol is characterized by higher concentrations of crustal material but lower concentrations of organic aerosol, elemental carbon and ammonium nitrate (Pey et al., 2009). Nevertheless, relatively high  $\text{PM}_{2.5}$  concentrations of carbonaceous aerosol and sulfate transported from populated coastal areas are regularly recorded, especially during winter anticyclonic episodes and summer midday PM highs (Pey et al., 2009, 2010). The organic carbon (OC) to EC ratio found (14 in summer, 10 in winter) pointed to the influence of biogenic emissions, secondary organic aerosol (SOA) formation favoured by high ozone concentrations and insolation, and the intensive recirculation of aged air masses (Pey et al., 2009; Querol et al., 2013).

The sources of organic aerosol in the regional background site of Montseny were studied in two intensive campaigns, using off-line  $^{14}\text{C}$  analysis (Minguillón et al., 2011), aerosol mass spectrometers (AMS) (Minguillón et al., 2011; Crippa et al., 2014) and organic tracers (Alves et al., 2012; Van Drooge et al., 2012). Minguillón et al. (2011) found that the contribution of fossil fuel combustion sources (mainly road traffic emissions) to OC at Montseny was 31 and 25 % in winter and summer, respectively, and that 85 % of this fossil OC was secondary. The contribution of biomass burning emissions was relatively low when compared with other regional background sites in Europe and was estimated to be 21 and 12 % of the total OC in winter and summer, respectively. Alves et al. (2012) concluded that the anthropogenic input may be associated with the transport of aged air masses from

the surrounding industrial and urban areas, which superimpose the locally originating biogenic hydrocarbons.

Besides these studies, a long time series of organic aerosol data has not been analysed in Montseny. To this end, the newly developed Aerosol Chemical Speciation Monitor (ACSM) would be suitable (Ng et al., 2011b), as opposed to the use of AMS, which cannot operate by itself and therefore is usually employed around the world for periods of only about 1 month. Nevertheless, due to its recent implementation, some studies based on ACSM data are found in the literature (Ng et al., 2011b; Shaw et al., 2012; Sun et al., 2012; Budisulistiorini et al., 2013; Canonaco et al., 2013, 2014; Carbone et al., 2013; Sun et al., 2013a, b; Takahama et al., 2013; Bougiatioti et al., 2014; Petit et al., 2015; Ripoll et al., 2015a).

The present study aims at interpreting a 1-year time series of inorganic and organic compounds in the submicron aerosol in the regional WMB, with a special focus on their evolution throughout the year as a function of the concatenation of different atmospheric scenarios. The different types and origins of OA are also investigated. To this end, an ACSM was deployed for 1 year in the regional background site of Montseny (MSY), according to the schedule planned within the Aerosols, Clouds, and Trace gases Research Infrastructure (ACTRIS) Network project. Moreover, a validation of the ACSM data is carried out by a comparison with co-located instruments both in real time and off-line.

## 2 Methodology

### 2.1 Sampling site

The MSY station ( $41^\circ 46' 46''$  N,  $02^\circ 21' 29''$  E; 720 m a.s.l.) is located in the Montseny natural park, in a densely forested area, 50 km to the N–NE of the Barcelona urban area, and 25 km from the Mediterranean coast. The station is located on the upper slopes of a valley extending perpendicularly from the Catalan pre-coastal ranges to the coast. The site is relatively far from urban and industrial areas, but it can be affected by anthropogenic emissions transported from populated and industrialized areas under specific meteorological conditions. The MSY station is in the ACTRIS Network (formerly EUSAAR, European Supersites for Atmospheric Aerosol Research), is a Global Atmosphere Watch (GAW) site, and is part of the network of the Institute of Environmental Assessment and Water Research (IDAEA-CSIC) and of the air quality monitoring network of the Department of Environment of the Autonomous Government of Catalonia.

The prevailing atmospheric dynamics has been described elsewhere (Pérez et al., 2008; Pey et al., 2009). Briefly, in winter the location of the Azores high-pressure system favours the entry of clean Atlantic air masses into the WMB which replace the existing air masses, leading to a decrease in pollutants. In summer, the very weak pressure gradients re-

sult in local circulations dominating the atmospheric dynamics with the consequent accumulation of pollutants (Millán et al., 1997). The climate is typical Mediterranean, with warm summers, temperate winters and irregular precipitation rates during the year.

The daily classification of meteorological episodes affecting MSY during the study period was made as described in Pérez et al. (2008), leading to the following types of scenario: Atlantic advection, north African, Mediterranean, European, regional and winter anticyclonic episodes. The frequency of each type of scenario for each of the months of the study period is shown in Fig. S1 in the Supplement.

## 2.2 ACSM settings, calibrations and data processing

An ACSM was deployed from June 2012 to July 2013, according to the ACTRIS schedule, to measure non-refractory submicron aerosol species (organics, nitrate, sulfate, ammonium and chloride) in real time (Ng et al., 2011b). Briefly, the instrument uses an aerodynamic lens to sample and focus submicron particles (75–650 nm) into a narrow particle beam (Liu et al., 2007), with a flow of approximately  $85 \text{ cc min}^{-1}$ . The beam is transmitted into the final of three vacuum chambers, where particulate matter is flash-vaporized on a hot oven ( $600^\circ\text{C}$ ), ionized by hard electron impact ionization (70 eV) and subsequently detected using a commercial quadrupole mass spectrometer. The concentration of the aforementioned species is calculated based on the measured aerosol mass spectra. The concentration of a given species is calculated based on the addition of the ion signals at each of its mass spectral fragments and its ionization efficiency (IE) (Canagaratna et al., 2007). Since the calibration of IEs for all ambient species is not feasible, the relative ionization efficiency (RIE) (compared to that of nitrate) is used for different species.

Thus, the mass calibration of the ACSM is based on determining the instrument response factor (RF) using ammonium nitrate calibration aerosol (Ng et al., 2011b). In this study, an atomizer (TSI, constant output atomizer model 3076) was used for primary aerosol generation, followed by a silica gel diffusion dryer, a scanning mobility particle sizer (SMPS) system (model TSI 3936), comprised of an electrostatic classifier (model TSI 3080) with a differential mobility analyser (DMA, model TSI 3081), and a condensation particle counter (CPC, TSI 3772). Monodisperse 300 nm ammonium nitrate aerosol particles were generated for the calibration. The calibration comprised a range of nitrate concentrations from 0 to  $15 \mu\text{g m}^{-3}$ , which were achieved by diluting the generated aerosol. RIE for ammonium was directly determined from the ammonium nitrate calibration.

Several calibrations were carried out through the sampling period, and average values for nitrate IE and RIE for ammonium were used for the whole data set. After several tests around the world, more experience has been gained regarding the performance of the ACSM. Hence, RIE for sulfate has

been shown to vary from instrument to instrument, and therefore the default value (1.2) (Ng et al., 2011b) cannot be directly used. This information was not known until our ACSM was no longer at the MSY station, and hence, sulfate RIE was determined by carrying out the aforementioned calibration exercise with ammonium sulfate monodisperse aerosol in Barcelona. The sulfate RIE value found was very close to the default value, and hence 1.2 was used for the current data set. The default RIE for organics (1.4) (Ng et al., 2011b) has been used, although some discussion about this can be found in Sect. 3.1.

The ACSM was connected to a general inlet equipped with a nafion drier to maintain the RH below 40 %, although technical problems resulted in some periods (about 50 % of the data points) with uncontrolled RH. The ACSM was run with a time resolution of approximately 30 min, resulting from the following settings: 24 scans (alternating between 1 sample and 1 filtered scan) per data point with a scan speed of  $500 \text{ ms amu}^{-1}$ . The data acquisition software provided by Aerodyne Research (version 1.4.2.5 from the beginning of the study to 18 December 2012 and version 1.4.3.8 for the rest of the period) was used to process the measurements. The data were analysed with the ACSM data analysis software version 1.5.3.2 (Aerodyne Research Inc.) written in Igor Pro (WaveMetrics, Inc., Lake Oswego, OR, USA). A correction for the instrument performance limitations was applied to the data set based on the inlet pressure and  $\text{N}_2$  signal. The aerosol mass concentrations were then corrected for particle collection efficiency (CE) following the Middlebrook approach (Middlebrook et al., 2012). 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 the view in, e.g., Hawkins et al. (2010).

## 2.3 Additional measurements and instrumentation

Submicron particulate matter ( $\text{PM}_{10}$ ) 24 h samples were collected on quartz fibre filters (Pallflex 2500QAT-UP) using DIGITEL (DH-80) high-volume ( $30 \text{ m}^3 \text{ h}^{-1}$ ) samplers with a  $\text{PM}_{10}$  impactor inlet. The sampler, and therefore the collected samples, was kept inside a container with controlled temperature (between  $24$  and  $26^\circ\text{C}$ ). Samples were collected every 4 days. Gravimetric  $\text{PM}_{10}$  determination was carried out by weighing the filters before and after sampling, after stabilization in a conditioned room ( $20^\circ\text{C}$  and 50 % relative humidity). Chemical off-line analyses were carried out. A quarter of the filter was acid digested ( $\text{HNO}_3 : \text{HF} : \text{HClO}_4$ ), and the resulting solution was analysed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) for the determination of major elements, including S, from which the sulfate concentration was calculated. Another quarter of the filter was water extracted to determine the nitrate, sulfate and chloride concentrations by ion chromatography and the ammonium concentrations with an ion selective electrode. OC concentrations were determined by thermal-optical methods

using a Sunset instrument and following the EUSAAR\_2 thermal protocol (Cavalli et al., 2010). Blank filters were analysed together with the samples, and concentrations were subtracted from those found in the samples in order to calculate the ambient concentrations.

PM<sub>1</sub> 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). Equivalent black carbon (BC) mass concentrations (Petzold et al., 2013) were measured with a 1 min time resolution by a multi-angle absorption photometer (MAAP, model 5012, Thermo) using a PM<sub>10</sub> inlet and using the default mass absorption cross section (MAC) from the instrument software (6.6 m<sup>2</sup> g<sup>-1</sup>). Particle number size distributions (9–820 nm) were measured by an 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.

Wind direction and speed, solar radiation, temperature, relative humidity and precipitation were recorded using conventional instruments, and hourly data can be seen in Fig. S2.

## 2.4 Source apportionment of OA

The source apportionment of the organic fraction can be investigated by applying positive matrix factorization (PMF) (Paatero and Tapper, 1994) to the organic mass spectra using the multilinear engine (ME-2) (Paatero, 1999). Both methods describe the measurements with a bilinear factor model:

$$x_{ij} = \sum_{k=1}^p g_{ik} f_{kj} + e_{ij}, \quad (1)$$

where  $x_{ij}$  is the  $j$ th species ( $m/z$ ) concentration measured in the  $i$ th sample,  $p$  is the number of sources,  $g_{ik}$  is the contribution of the  $k$ th source to the  $i$ th sample,  $f_{kj}$  is the concentration of the  $j$ th species in the  $k$ th source (mass spectra) and  $e_{ij}$  is the residual associated with the  $j$ th species concentration measured in the  $i$ th sample. The values  $g_{ik}$  and  $f_{kj}$  are adjusted until a minimum for the objective function  $Q$  for a given number of factors  $p$  is found:

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

where  $\sigma_{ij}$  is the user-defined uncertainty for the  $j$ th species in the  $i$ th sample.

With the ME-2, the user can introduce a priori information about sources, e.g. using the so-called  $a$  value approach. Hence, the user inputs a factor profile and a constraint defined by the  $a$  value, which determines the extent to which the output profile can differ from the profile fed to the model. This can be done for one or more factors.

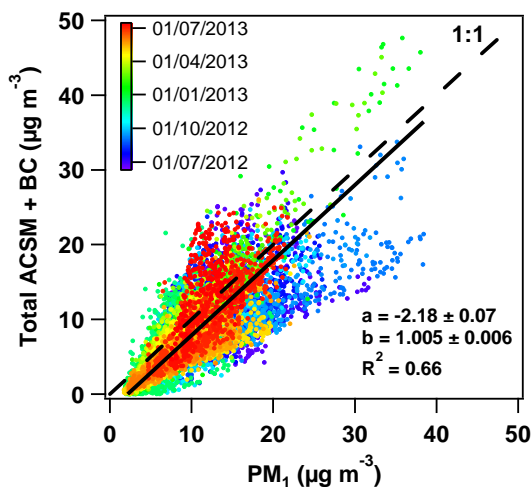
In the present study the source apportionment to OA was performed applying ME-2 and using the toolkit SoFi (Source Finder) version 4.7 described in Canonaco et al. (2013). The ME-2 was applied separately for the warm and cold periods in this study, given the expected differences among them. The warm period was defined as a period with > 70 % of the days with average  $T > 19$  °C, hourly max  $T > 24$  °C and hourly min  $T > 15$  °C, which includes 14 June to 9 October 2012. The cold period was defined as a period with > 70 % of the days with average  $T < 10$  °C, hourly max  $T < 13$  °C and hourly min  $T < 8$  °C and includes 28 October 2012 to 7 April 2013. Only  $m/z \leq 100$  were used, for several reasons: (a) the signals of  $m/z > 100$  account for a minor fraction of the total signal (2 % on average), (b) the  $m/z > 100$  have larger uncertainties and (c) the large interference of naphthalene signals (at  $m/z$  127, 128 and 129) is avoided. The error matrix was calculated by the aforementioned customized software, which downweights the  $m/z$  masses calculated from the  $m/z$  44 signal. Moreover,  $m/z$  with signal-to-noise ratio ( $S/N$ ) below 0.2 were downweighted by a factor of 10, and those with  $S/N$  between 0.2 and 1 were downweighted by a factor of 2.

## 3 Results and discussion

### 3.1 Comparison of ACSM data with other measurements

This is one of the few studies, together with Ripoll et al. (2015a), that compare ACSM data with off-line PM<sub>1</sub> measurements. Most of the studies found in the literature comparing ACSM data with off-line measurements are based on the PM<sub>2.5</sub> fraction for the off-line measurements. In this study we use PM<sub>1</sub> measurements, avoiding the tail of the coarse mode that the PM<sub>2.5</sub> fraction includes and hence being closer to the size range measured by the ACSM (75–650 nm).

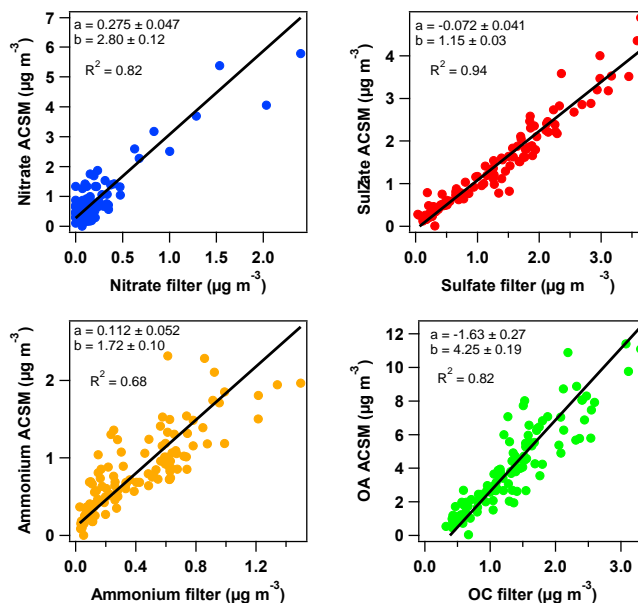
The sum of the ACSM component concentrations and the BC concentrations measured by the MAAP was compared with PM<sub>1</sub> concentrations determined by the optical particle counter, resulting in a strong correlation (squared Pearson correlation coefficient  $R^2 = 0.66$ ) and a slope very close to unity (1.005) (Fig. 1). The application of a time-dependent CE to the ACSM data based on the Middlebrook approach (Middlebrook et al., 2012) resulted in a better fit compared to the use of a constant CE = 0.5 used in several studies (which resulted in a slope of 0.913 and a  $R^2 = 0.65$ ). Hence, the time-dependent CE application is considered more suitable for the present study. 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 (Fig. S3). 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) (Fig. S4).



**Figure 1.** ACSM components + BC concentrations vs.  $PM_{10}$  measured by the optical counter, coloured according to the sampling time (dd/mm/yyyy). Line and parameters correspond to least orthogonal distance fit ( $y = a + bx$ ). The wild fire period is excluded from the fit.

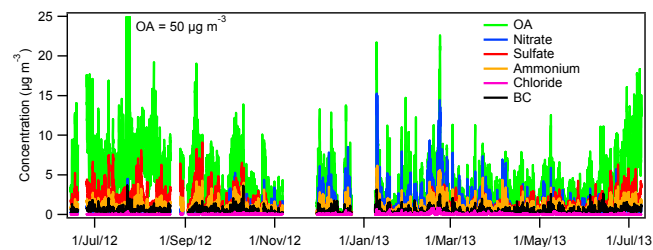
Moreover, daily averages of ACSM component concentrations were calculated and compared to off-line measurements from 24 h  $PM_{10}$  samples (Fig. 2). All the species, except for chloride, showed strong correlations ( $R^2$  of 0.68, 0.82 and 0.94 for ammonium, nitrate and sulfate, respectively). Chloride concentrations were below or close to detection limits for both ACSM and off-line analysis, which may be the cause for the discrepancies found. Such discrepancies were also found in other studies (Budisulistiorini et al., 2014). For each of the strongly correlated species, the slopes (ACSM vs. off-line measurements) were different. Whereas the slope was close to unity for sulfate (1.15), it was higher for ammonium (1.72) and much higher for nitrate (2.80). Ultimately, this discrepancy remains unexplained, although a possible cause is the volatilization of ammonium nitrate from the filters. Nevertheless, the volatilization of ammonium nitrate is expected to be low given that the samples are kept in controlled conditions (24–26 °C) as described in the methods section. Moreover, if random volatilization occurred, the correlation coefficients found between ACSM and filters would be lower. The apparent discrepancy between the slope for total  $PM_{10}$  (ACSM+BC vs.  $PM_{10}$  from the optical particle counter corrected with gravimetric measurements, close to unity) and the slopes for the different components ( $> 1$ ) is attributed to the undetermined fraction of  $PM_{10}$  mass in the filters. Thus, whereas the ACSM+BC concentrations are strictly the sum of the components, the  $PM_{10}$  gravimetric concentrations include a fraction of undetermined mass, partially attributed to water (Fig. S5).

For organic aerosol a strong correlation was found ( $R^2 = 0.82$ ), and the high slope obtained (4.25) may be interpreted as the ratio between organic matter (OM) and OC (OM-to-



**Figure 2.** ACSM component concentrations vs. 24 h samples concentrations. Lines and parameters correspond to least orthogonal distance fits.

OC ratio), since the ACSM measures OA and the off-line measurements determined OC. 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 discussed later (Sect. 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 (a) the underestimation of OC due to the loss of semi-volatile organic compounds from the filters and (b) the overestimation of OM by the ACSM due to an underestimation of the RIE for organics. The first reason is expected to be less likely given the strong correlation found between OA and OC (which would not be so if random volatilization occurred) and given that the samples are kept at controlled conditions, as formerly explained, hence reducing the possible volatilization. Previous studies also found higher than expected OM-to-OC ratios when comparing ACSM OA with off-line OC measurements. Budisulistiorini et al. (2014) found OM-to-OC ratios of 4.85 and 3.85 in summer and fall, respectively. Ripoll et al. (2015a) found an OM-to-OC ratio of 3.39 for a 1-year sampling period. This topic is currently being investigated by the ACSM manufacturer. The calculation of the OM-to-OC ratio from the  $f_{44}$  based on Aiken et al. (2008) was not carried out given that it is not suitable for ACSM instruments, as recently shown by an intercomparison of 13 Q-ACSM instruments (Fröhlich et al., 2015).

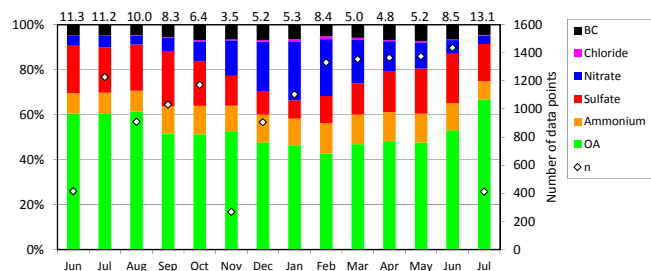


**Figure 3.** Time series of ACSM components and BC concentrations during the whole study period.

### 3.2 Time series and average composition of submicron aerosol – seasonal variation

The average concentration (P25, P75) of the ACSM components plus BC concentrations during the study period was  $7.3 \mu\text{g m}^{-3}$  (3.1, 10.2). The highest concentrations were measured during the warm periods (average  $10.3 \mu\text{g m}^{-3}$ ), defined as the periods with most of the days with average  $T > 20^\circ\text{C}$  (from 14 June to 9 October 2012 and from 13 June to 9 July 2013). The lowest concentrations were recorded during the cold period (average  $5.8 \mu\text{g m}^{-3}$ ), which includes a period with most of the days with average  $T < 13^\circ\text{C}$  (from 28 October 2012 to 7 April 2013) (Fig. 3). The average monthly concentrations, following the described variation, can be seen in Fig. 4. The seasonal variation in the concentrations is in agreement with that observed during a long time period (2002–2010) by Cusack et al. (2012). The summer increase is associated with the recirculation of air masses that prevent air renovation, the low precipitation (Fig. S2) and the formation of secondary aerosols enhanced by the maximum solar radiation (Fig. S2). The lower winter concentrations can be explained by the high frequency of Atlantic advections (Fig. S1) and the higher precipitation rates, although occasional high concentrations are attributed to winter anticyclonic scenarios (Pey et al., 2010). The seasonal variation in  $\text{PM}_{10}$  concentrations at MSY is also influenced by the evolution of the boundary layer height, which is lower during wintertime and increases during summertime, especially during the hours around noon. Changes in the origin of air masses also determined the seasonal variation in  $\text{PM}_{10}$  concentrations.

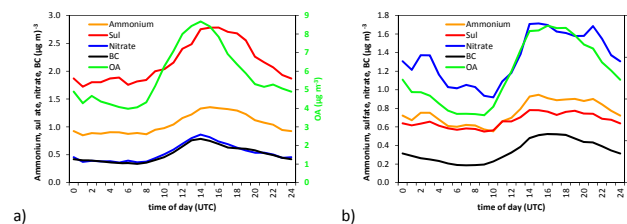
On average, the most abundant component was OA ( $3.8 \mu\text{g m}^{-3}$ ), followed, in this order, by sulfate ( $1.3 \mu\text{g m}^{-3}$ ), ammonium ( $0.8 \mu\text{g m}^{-3}$ ), nitrate ( $0.8 \mu\text{g m}^{-3}$ ), BC ( $0.4 \mu\text{g m}^{-3}$ ) and chloride ( $< 0.1 \mu\text{g m}^{-3}$ ). The OA contribution varied throughout the year, reaching 60 % of the total  $\text{PM}_{10}$  in the summer period (June, July and August) and decreasing progressively down to 43 % in February (Fig. 4). The contribution of sulfate followed the same seasonal variation, from about 20 % in the warmer months to about 8 % in the colder months. The nitrate contribution showed an inverse trend, with higher relative contributions in the winter



**Figure 4.** Monthly relative chemical composition of submicron aerosol. The numbers at the top of each bar represent the average monthly concentration.  $n$  is the number of data points for each month (right axis).

and much lower concentrations in summer. These seasonal variations were already observed in previous studies using off-line filter sampling (Pey et al., 2009; Ripoll et al., 2015b) and can be attributed to a higher SOA contribution, the favoured formation of sulfate and the nitrate gas–aerosol partitioning leading to the vaporization of ammonium nitrate during the warmer period.

When investigating the diurnal patterns, it is observed that OA, nitrate and BC concentrations reach their maximum at around 14:00 UTC in summer, whereas sulfate and ammonium show a delayed increase in their concentrations, peaking at around 16:00 UTC (Fig. 5). This shift may be due to the different origin of each component. Whereas the OA, nitrate and BC are transported with the breeze from the populated areas and the valley towards the regional background site, sulfate can also be transported from further away, i.e. from over the Mediterranean Sea, due to shipping emissions. Later in the day, when the breeze develops in the opposite direction (from inland towards the coast), the concentrations of OA, BC and nitrate decrease, whereas the sulfate and ammonium concentrations remained high for a longer time (until about 19:00 UTC). This is due to the more regional character of ammonium sulfate, which is present in a wider area due to its longer lifetime in the atmosphere (Seinfeld and Pandis, 2006) and hence remains at MSY for longer. In addition to the transport of pollutants, local SOA can be formed (see Sect. 3.5 for discussion). Specific episodes may differ from this average behaviour owing to specific atmospheric characteristics, for which sulfate concentrations increase simultaneously with OA, but the most common variation is the one described here. On the other hand, in winter, all the components show an increase at around 15:00 UTC and concentrations remain high until around 22:00 UTC, when they start to decrease to reach a minimum around 09:00 UTC (Fig. 5). This simultaneous variation indicates that the pollutants are transported from the nearby polluted areas to MSY with the breeze.

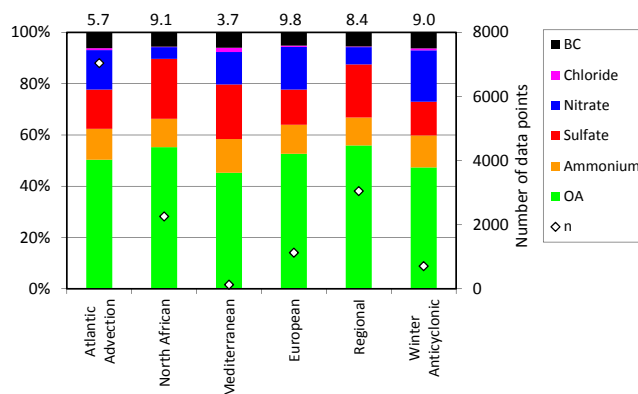


**Figure 5.** Average daily pattern for (a) the warmer and (b) the colder periods. Note that OA is plotted on the right axis.

### 3.3 Influence of the type of scenario on submicron aerosol

The total PM<sub>1</sub> concentrations were investigated as a function of the type of scenario, finding the lowest concentrations during Mediterranean episodes and Atlantic advections and the highest during northern African outbreaks, European episodes and winter anticyclonic episodes (Fig. 6). Some differences in the relative chemical composition as a function of the type of scenario were found (Fig. 6). OA and sulfate relative contributions were higher under regional and northern African episodes. This may be due to the higher formation of secondary aerosols enhanced by the higher temperature and solar radiation during these episodes (see additional discussion about formation of SOA in Sect. 3.5). Moreover, the higher sulfate concentrations under regional episodes may also be due to the enhanced regional mixing, as shown by the flatter diurnal pattern of this pollutant (Fig. S6). Sulfate relative contribution was also high when Mediterranean air masses affected MSY, probably owing to the impact of shipping emissions. On the other hand, nitrate relative contribution was found to be higher for winter anticyclonic and European episodes. For both cases the colder weather compared to the rest of the year is partly responsible for the higher nitrate concentrations. During winter anticyclonic episodes, the stagnant conditions favouring the accumulation of polluted air masses that are transported from the Barcelona metropolitan area towards MSY may also be responsible for the high nitrate concentrations (Pey et al., 2010). Note that this transport takes place later in the day than in warm conditions, thus reaching maximum concentrations between 15:00 and 22:00 UTC, and that the day–night difference is much higher than for other scenarios (Fig. S6). During European episodes, the higher nitrate concentration can be attributed to the long-range transport of nitrate from Europe to the study area, although this type of episodes often take place under anticyclonic conditions and hence the nitrate may have a local origin at lower heights, whereas European nitrate is transported at higher altitudes, as shown by Ripoll et al. (2015b).

The relative chemical composition as a function of the total concentration was also investigated, but no clear patterns were identified, meaning that there is no prevalent component for low or for high concentrations (Fig. S7).



**Figure 6.** Relative chemical composition of submicron aerosol as a function of the type of scenario. The numbers at the top of each bar represent the average concentration for each type of scenario.  $n$  is the number of data points for each type of scenario (right axis).

### 3.4 Wildfire episode

A wildfire took place from 22 to 26 July 2012 (Fig. 7) at 100 km to the NE of MSY, affecting a wide area (Fig. S8). It resulted in an average ACSM components + BC concentrations of  $16.5 \mu\text{g m}^{-3}$  over the 5-day period. The components whose concentrations increased significantly were mainly OA, nitrate and BC, reaching 30 min values of 50, 4.5 and  $3.6 \mu\text{g m}^{-3}$ , respectively, which are 9, 8 and 7 times higher than their respective summer averages. The average relative concentration during this episode was dominated by OA (73 %).

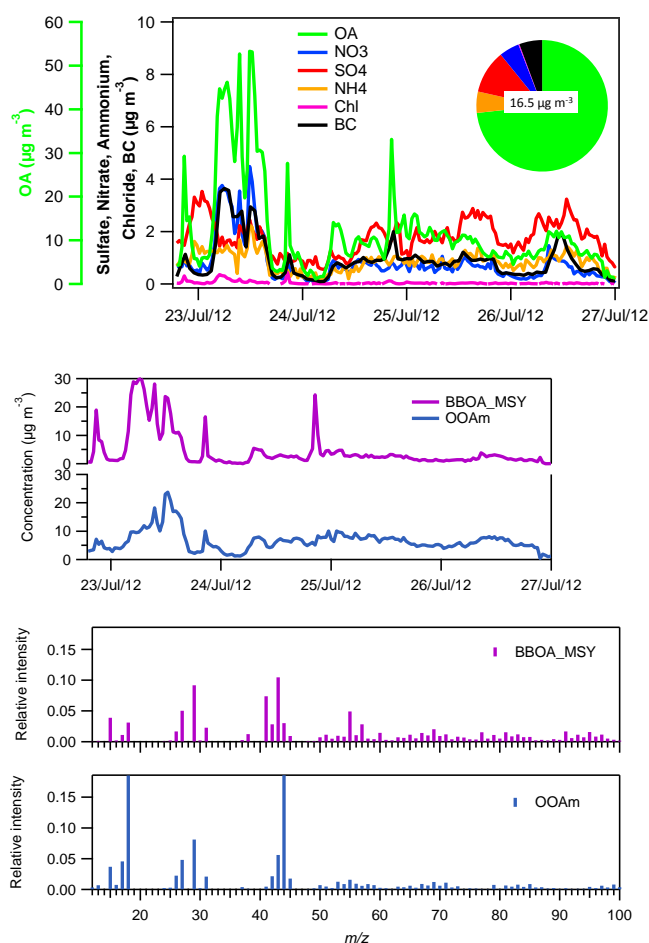
In order to investigate the wildfire source, an unconstrained source apportionment (PMF) of the organic aerosol fraction during this episode was carried out. The PMF resulted in two factors, one representing the fresh biomass burning organic aerosol (BBOA, referred to as BBOA\_MSY) and another one interpreted as the mix of other OA sources and aged BBOA, referred to as OOAm (oxygenated OA, 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  $\text{CO}_2^+$ ) 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 a differentiation between 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 made up 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 data sets (Ng et al., 2011a) (Fig. 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 differences were found: mainly, our profile has higher  $m/z$  43 and  $m/z$  41 signals and lower  $m/z$  60 (Fig. S9). This BBOA\_MSY mass spectrum is considered specific to the study area, and hence it can later be used for other studies in the region to feed 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.

### 3.5 Source apportionment of organic aerosol

The source apportionment of organic aerosol was carried out separately for the warmer period (14 June to 9 October 2012) and the colder period (28 October 2012 to 7 April 2013). The days of the wildfire event were excluded from the warmer period data set. The separation into two seasons was done to better characterize the profiles of the different sources, especially the different types of OOA, given that it is expected to vary throughout the year.

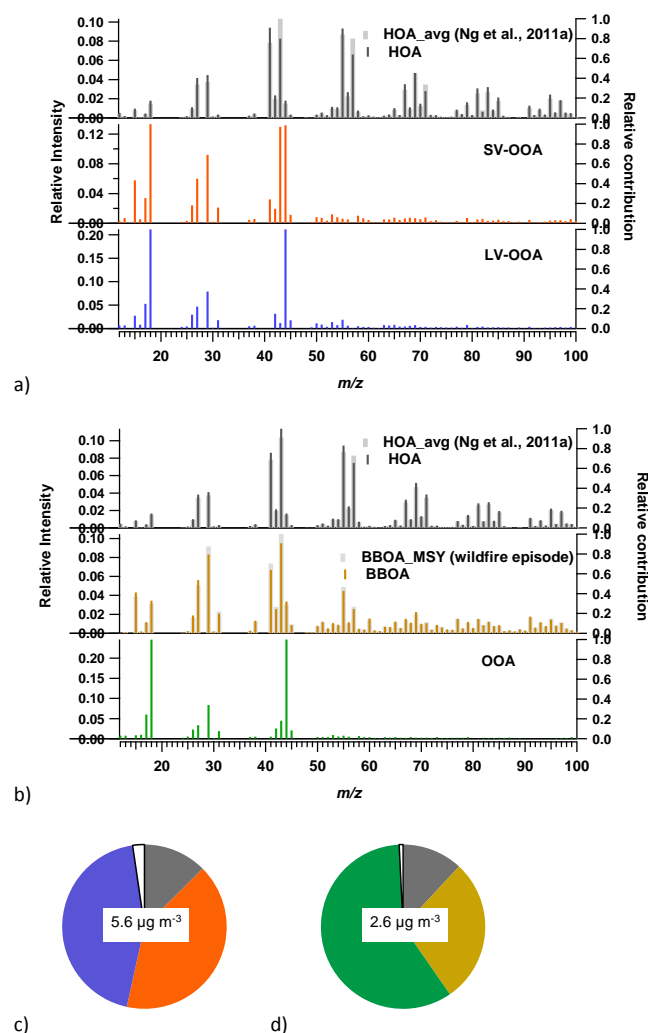
The application of ME-2 to the warmer period resulted in a solution with three factors: a hydrocarbon-like OA (HOA), a semi-volatile oxygenated OA (SV-OOA) and a low-volatile oxygenated OA (LV-OOA). This solution was chosen based on several tests with a different number of factors and different  $a$  values for the constrained factors, taking into account the correlations with external data, the diurnal patterns and the residuals and 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 data sets (Ng et al., 2011a). An  $a$  value range from 0.05 to 0.3 was explored and an  $a$  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  $a$  value) and the physically meaningful profiles of the whole solution (i.e. resulting from an assessment of the profiles of the LV-OOA and SV-OOA factors). Hence, the  $a$  value 0.05 did not reach convergence, and the  $a$  value 0.1 resulted in OOA factors that were not well resolved. BC concentrations correlated moderately with the HOA of the chosen solution (squared Pearson



**Figure 7.** (a) Time series of ACSM components and BC concentrations and pie chart of the average chemical composition during the wildfire from 22 to 26 July 2012. (b) Time series of the contribution of the BBOA\_MSY and OOAm sources identified by PMF. (c) Source profile of the BBOA\_MSY and OOAm sources.

coefficient  $R^2 = 0.51$ ; Table S1 in the Supplement). The SV-OOA shows a higher 43 : 44 ratio compared to the LV-OOA, together with a lower  $f_{44}$ ; these are the main differences between these two profiles (Fig. 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  $f_{60}$  registered in the present study in summer (Fig. 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. The correlations of the two OOA factors with external secondary pollutants are not very high (LV-OOA with ammonium shows  $R^2 = 0.43$ , LV-OOA with sulfate shows  $R^2 = 0.34$  and SV-OOA with nitrate shows  $R^2 = 0.16$ ; Table S1). Nevertheless, the source profiles are well defined. The four-factor solution was investigated and resulted in a split of the LV-OOA factor. The residuals of the three-factor solution showed an increase between 12:00 and 15:00 (which

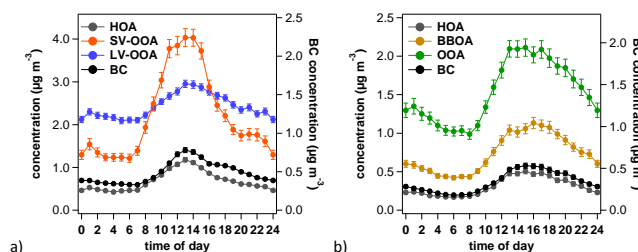




**Figure 8.** Mass spectral profiles of the organic sources identified for (a) summer and (b) winter. Average contribution of the organic sources to total OA for (c) summer and (d) winter. The white fraction of the pie charts corresponds to unexplained mass.

did not disappear in the four-factor solution), hence indicating the difficulty in explaining the variation of the OA during the middle hours of the day. This pattern was also observed for the  $m/z$  43 variable residuals, whereas it was not observed for other variables. Therefore, the difficulty in the OA explanation may be more related to the SOA formation processes rather than to primary OA sources. Further details on the chosen solution can be found in the Supplement (Figs. S11 to S15).

During the warmer period, the HOA accounted for 13 % of the total OA ( $0.7 \mu\text{g m}^{-3}$ ), whereas the LV-OOA and the SV-OOA accounted for 44 % and 41 % ( $2.5$  and  $2.3 \mu\text{g m}^{-3}$ ), respectively; hence, there remained 2 % of unexplained OA mass (Fig. 8c). The time series is shown in Fig. S16. As explained before, the location and meteorological conditions at MSY result in an increase in pollutants concentrations start-



**Figure 9.** Average daily patterns of the organic-source contributions and BC concentrations for (a) summer and (b) winter. Error bars represent standard deviations.

ing in the mid-morning, caused by breeze transport from populated areas to the regional site. This variation is clearly observed for BC (Fig. 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 only be 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 in SV-OOA 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 (Fig. 9) points to a more regional and well-oxidized aerosol, which could be interpreted as the regional background SOA. The difference in the diurnal patterns between LV-OOA and SV-OOA is more evident during the regional episodes, evidencing the mixing of the background pollutants (LV-OOA) and the formation of SOA on site (part of the SV-OOA) (Fig. S17). 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 three factors: hydrocarbon-like OA (HOA), biomass burning OA (BBOA) and oxygenated OA (OOA) (Fig. 8b). A solution with two OOA factors was investigated, but it was not meaningfully interpretable. Probably the small temperature range variation in winter does not result in enough diurnal variation in  $f_{43}$  and  $f_{44}$  to separate the OOA into SV-OOA and LV-OOA. As per the warmer period, a solution was ultimately chosen based on the strategy described by Crippa et al. (2014) and Canonaco et al. (2013). For coherence with the warmer period, the HOA factor was based on an average HOA factor (HOA\_avg) from different data sets (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 concentra-

tions found for different  $a$  value tests, on the source profiles obtained for the rest of the sources (ensuring that they were meaningful), and on a preference for relatively low  $a$  values to avoid the mixing of OOA sources into the HOA source. The HOA contribution of the chosen solution shows a relatively strong correlation with BC concentrations (squared Pearson coefficient  $R^2 = 0.70$ ; Table S1). 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. It was decided that the BBOA factor should be constrained based on the  $f_{60}$  signal, which was above the aforementioned threshold of 0.003 (Fig. S10). It was based on the BBOA\_MS\_Y profile found for the wildfire that took place during this study, constrained with an  $a$  value of 0.1. The  $a$  value was chosen using the following criteria: preference for a low  $a$  value, given that the anchor profile used was site-specific; lack of a diurnal pattern for residuals for the  $m/z$  60; 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\_MS\_Y, 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  $f_{44}$  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 sulfate ( $R^2 = 0.49$ ), relatively strongly with nitrate ( $R^2 = 0.73$ ) and more strongly with ammonium ( $R^2 = 0.79$ ; Table S1). Further details on the chosen solution can be found in the Supplement (Figs. S11 to S15).

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 28 % ( $0.7 \mu\text{g m}^{-3}$ ) of the total OA, respectively, with only 1 % of the OA mass remaining unexplained (Fig. 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  $\text{PM}_{10}$  samples (Fig. S18), 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 high-resolution time of flight 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 dif-

ferent sampling periods (the current study included November 2012–March 2013, whereas the previous study only included March 2009), to the inclusion 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 5 years.

The average daily pattern shown by the different OA sources in winter (Fig. 9) resembles that of BC, nitrate, sulfate and ammonium (Fig. 5), with an increase in pollutant concentrations starting at around 10:00 UTC and reaching high concentrations at around 13:00 UTC. No significant differences in the daily pattern other than the different concentrations were observed for different meteorological episodes (Fig. S17). This daily increase is attributed to the transport with the breeze from populated areas to the mountain site. This variation is observed for all the components, and therefore the local formation of SOA is deduced to be low in winter.

#### 4 Conclusions

The deployment of an ACSM at the regional background site of Montseny during 1 year allowed for the characterization of  $\text{PM}_{10}$  composition and its variation as a function of time of the year and atmospheric scenarios. The OA sources were also identified and studied.

Strong correlation ( $R^2 = 0.66$ ) was found between total mass determined by ACSM components + BC and  $\text{PM}_{10}$  determined by an optical particle counter with a slope near unity. The suitability of the application of a composition-dependent CE was confirmed.

Strong correlations were found between the ACSM measurements and off-line measurements (filters) for sulfate ( $R^2 = 0.93$ ), ammonium ( $R^2 = 0.68$ ) and nitrate ( $R^2 = 0.82$ ). Nevertheless, the slopes differ more than 20 % from unity for nitrate and ammonium.

The comparison of the OA measured by the ACSM with the OC measured in filter samples points to a current underestimation of the RIE established for OA.

A wildfire significantly affected the organic aerosol concentrations. The source profile of fresh BBOA for this specific episode was characterized, and it resembles those from other studies. The BBOA contribution in winter correlates with the  $\text{PM}_{10}$  potassium concentrations.

OA was the major component of submicron aerosol on average and especially during the warm periods. Three organic sources were identified by PMF in summer (HOA, SV-OOA and LV-OOA) and three in winter (HOA, BBOA and OOA). SOA was the major constituent of the OA at MSY, making up more than 80 % of total OA in summer and about 60 % in winter. The in situ formation of SOA in summer, occurring around midday, was estimated to be  $1.1 \mu\text{g m}^{-3}$  on average (20 % of OA).

Sulfate concentrations were higher in summer, while nitrate concentrations were higher in winter due to environmental conditions (temperature, relative humidity and solar radiation, among others). Sulfate originates from a wider area and is affected by the shipping emissions from the Mediterranean, while the rest of the components may have an origin that is nearer.

As typical for mountain sites, all the pollutants were affected by the general breeze regime, leading to an increase from mid-morning until the afternoon and a decrease until the evening.

**The Supplement related to this article is available online at doi:10.5194/acp-15-6379-2015-supplement.**

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