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Long-term real-time chemical characterization of submicron aerosols at Montsec (Southern Pyrenees, 1570 m a.s.l.)

A. Ripoll[1,2], M. C. Minguillón[1], J. Pey[3], J. L. Jimenez[4], D. A. Day[4], X. Querol[1], and A. Alastuey[1]

[1] Institute of Environmental Assessment and Water Research (IDAEA-CSIC), Jordi Girona 18–26, 08034, Barcelona, Spain
[2] Department of Astronomy and Meteorology, Faculty of Physics, University of Barcelona, Martí i Franqès 1, 08028, Barcelona, Spain
[3] Aix-Marseille Université CNRS, LCE FRE 3416, Marseille, 13331, France
[4] Department of Chemistry and Biochemistry, and Cooperative Institute for Research in the Environmental Sciences (CIRES), University of Colorado at Boulder, 80309, CO, USA

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Correspondence to: A. Ripoll (anna.ripoll@idaea.csic.es)

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Abstract

Real-time measurements of inorganic (sulfate, nitrate, ammonium, chloride and black carbon (BC)) and organic submicron aerosols from a continental background site (Montsec, MSC, 1570 m a.s.l.) in the Western Mediterranean Basin (WMB) were conducted for 10 months (July 2011–April 2012). An Aerosol Chemical Speciation Monitor (ACSM) was co-located with other on-line and off-line PM_1 measurements. Analyses of the hourly, diurnal, and seasonal variations are presented here, for the first time for this region.

Seasonal trends in PM_1 components are attributed to variations in: evolution of the planetary boundary layer (PBL) height, air mass origin, and meteorological conditions. In summer, the higher temperature and solar radiation increases convection, enhancing the growth of the PBL and the transport of anthropogenic pollutants towards high altitude sites. Furthermore, the regional recirculation of air masses over the WMB creates a continuous increase in the background concentrations of PM_1 components and causes the formation of reserve strata at relatively high altitudes. Sporadically, MSC is affected by air masses from North Africa. The combination of all these atmospheric processes at local, regional and continental scales results in a high variability of PM_1 components, with poorly defined daily patterns, except for the organic aerosols (OA). OA was mostly oxygenated organic aerosol (OOA), with two different types: semi-volatile (SV-OOA) and low-volatile (LV-OOA), and both showed marked diurnal cycles regardless of the air mass origin, especially SV-OOA. This different diurnal variation compared to inorganic aerosols suggested that OA components at MSC are not only associated with anthropogenic and long-range-transported secondary OA (SOA), but also with recently-produced biogenic SOA.

Very different conditions drive the aerosol phenomenology in winter at MSC. The thermal inversions and the lower vertical development of the PBL leave MSC in the free troposphere most of the day, being affected by PBL air masses only after midday, when the mountain breezes transport emissions from the adjacent valleys and plains to

the top of the mountain. This results in clear diurnal patterns of both organic and inorganic concentrations. Moreover, in winter sporadic long-range transport from mainland Europe is observed and leads to less marked diurnal patterns.

The results obtained in the present study highlight the importance of SOA formation processes at a remote site such as MSC, especially in summer. Additional research is needed to characterize the sources of SOA at remote sites.

1 Introduction

Earth's climate system is modulated by atmospheric aerosols. Submicron particles (< 1 µm in aerodynamic diameter) play a dominant role in both cloud formation and scattering or absorbing solar radiation (IPCC, 2013). The complexity of aerosol sources and processes results in an uncertainty in the radiative forcing of climate. Aerosol optical properties are connected to direct and indirect climate forcing effects, and they are dependent on particle composition. Moreover, aerosol composition may provide valuable information on aerosol sources and processes. Consequently, long-term measurements of PM_1 chemical composition are needed to better understand aerosol sources, to quantify their lifetime in the atmosphere and to constrain the uncertainties of their climatic influence.

Long-term PM_1 chemical composition measurements are relatively scarce both off-line and on-line. In the last decade, on-line PM_1 chemical composition measurements have been performed using aerosol mass spectrometers (AMS) at a number of locations. Measurements of on-line chemical composition are useful to study hourly variations and daily patterns. Most of these studies, however, correspond to short-term measurement campaigns (typically a month) (e.g. Crippa et al., 2014; Jimenez et al., 2009; Lanz et al., 2010; Ng et al., 2010; Zhang et al., 2007) given the intensive instrument maintenance required and the need of highly-qualified personnel for a good quality dataset.

In contrast to the use of the AMS in relatively short campaigns, the more recently developed Aerodyne Aerosol Chemical Speciation Monitor (ACSM) is becoming a widely used on-line instrument for long-term measurements of PM_1 chemical composition (Budisulistiorini et al., 2014; Canonaco et al., 2013; Petit et al., 2014; Tiitta et al., 2014). The ACSM provides mass concentration of inorganic and organic non-refractory submicron components via thermal vaporization and electron impact ionization mass spectrometry (Ng et al., 2011b). The ACTRIS (Aerosols, Clouds, and Trace gases Research InfraStructure) European network has included the ACSM as a reliable instrument, which will provide the opportunity to study long-term datasets of PM_1 chemical composition across the continent.

Recent publications have investigated most of the existing worldwide AMS databases (e.g. Crippa et al., 2013; Jimenez et al., 2009; Lanz et al., 2010; Ng et al., 2010; Zhang et al., 2007) and reflected a prevalence of organic aerosols (20 to 90 %) in the submicron fraction, largely independent of the region and type of environment. However, our knowledge on organic aerosol (OA) formation, sources, and atmospheric processing is still very incomplete, especially for secondary organic aerosols (SOA) formed from chemical reactions of gas-phase species (e.g. Donahue et al., 2014; Kroll and Seinfeld, 2008; Robinson et al., 2007; Volkamer et al., 2006). Recent progress has been made in identifying primary organic aerosols (POA) sources (e.g. Elbert et al., 2007; Zhang et al., 2005), but significant gaps still remain in our understanding on the atmospheric evolution of POA after emission (de Gouw and Jimenez, 2009). For these reasons, OA measurements and analysis are required to better understand its chemical evolution in the atmosphere.

The lack of long-term on-line PM_1 chemical composition measurements is especially evident in the Western Mediterranean Basin (WMB), which is characterized by particular atmospheric dynamics strongly influenced by its topography (Jorba et al., 2013; Millan et al., 1997). Over this region, elevated emissions of anthropogenic pollutants occur, arrival of natural and anthropogenic aerosols as a result of long-range transport from Africa and Europe is frequent (e.g. Pey et al., 2013; Querol et al., 2009; Ripoll et al., 2014b; Rodríguez et al., 2001), and accumulation and recirculation processes are frequently observed (Rodriguez et al., 2002). The sources and meteorological controls of PM in the regional background of the WMB have been recently investigated during the DAURE study (Pandolfi et al., 2014a) using an AMS and ^{14}C analyses (Crippa et al., 2014; Minguillón et al., 2011). Furthermore, Ripoll et al. (2014a) studied the PM_1 and PM_{10} chemical composition with daily time resolution in the continental and regional background environments in the WMB. In that study, a higher mineral contribution was identified in the continental background due to the preferential transport of African dust at high altitude layers and to the increased regional dust resuspension enhanced by the drier surface and higher convection. Nevertheless, aerosol chemical characterization with higher time resolution is needed to study the origin of specific PM components and the local and/or regional processes, in particular to exploit the information contained in diurnal cycles that is typically not accessible with off-line measurements.

In this study we deployed an ACSM at a high altitude site in southern Europe (Montsec, 1570 m a.s.l.), representative of the continental background conditions of the Western Mediterranean Basin (WMB) (Ripoll et al., 2014b). This environment is under free tropospheric (FT) influence most of the time, although it is exposed to regional pollutants during the summer time and/or under the influence of mountain breezes, and it is affected by trans-boundary incursions of natural and anthropogenic aerosols from Europe and North Africa (Ripoll et al., 2014a, b). Co-located on-line and off-line PM_1 measurements were also carried out to complement the ACSM dataset. Hence, the work presented here interprets the real-time variation of inorganic and organic submicron components during 10 months (July 2011–April 2012), and the types of OA are also studied. Special emphasis is placed on the analysis of diurnal pattern and seasonal variations of chemical components and the main factors influencing these variations.

Title Page
Abstract Introduction
Conclusions References
Tables Figures
◀| |▶
◀ ▶
Back Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

2 Methodology

2.1 Sampling site

Montsec (MSC) is a high altitude site (1570 m a.s.l.) located in the NE of the Iberian Peninsula (42°03′ N, 0°43′ E). It is found 50 km S of the Pyrenees and 140 km NW of Barcelona (Fig. S1). A detailed description of this site can be found in Ripoll et al. (2014b).

2.2 ACSM sampling and data analysis

The aerosol chemical speciation monitor (ACSM) (Aerodyne Research Inc.) was measuring continuously from July 2011 to April 2012. The ACSM provides real-time mass concentration of submicron particulate organics, nitrate, sulfate, ammonium and chloride via thermal vaporization and electron impact ionization, with detection by a quadrupole mass spectrometer and with unit mass resolution (Ng et al., 2011b). The mass concentration of a given species is determined from the sum of the ion signals at each of its mass spectral fragments and its Ionization Efficiency (IE) (Canagaratna et al., 2007). Since calibration of IE for all species is not feasible, IE for each of the species is expressed relative to the IE of the nitrate moiety (calibrated with pure ammonium nitrate particles) by the Relative Ionization Efficiency (RIE) (Jimenez et al., 2003). The ammonium nitrate calibration described by Ng et al. (2011b) was performed using an atomizer (TSI, Constant Output Atomizer Model 3076) for primary aerosol generation, followed by a silica gel diffusion dryer, a differential mobility analyzer (DMA) model TSI 3936, and a condensation particle counter (CPC, TSI 3772). Monodisperse 300 nm ammonium nitrate aerosol particles were used, covering a range of nitrate concentrations from 2 to 15 $\mu g\,m^{-3}$. An IE of 2.2×10^{-11} was obtained. The RIE for ammonium was measured as part of the ammonium nitrate calibration, and found to be 5.4. The RIE values used in this study for the rest of the species were those usually applied in AMS ambient concentrations: 1.4 for OA and 1.1, 1.2, and 1.3 for nitrate, sulfate, and chloride, respectively (Canagaratna et al., 2007). RIE for sulfate was experimentally determined after the end of the campaign and was found to be very close to 1.2 and hence the default value was used for the current dataset. A time resolution of 62 min was used as a result of 12 scans (1 open and 1 filtered) per data point with a scan speed of 1 s amu^{-1}.

The ACSM data were analyzed with the standard ACSM data analysis software version 1.5.3.2 (Aerodyne Research Inc.) written in Igor Pro 6 (WaveMetrics, Inc., Lake Oswego, OR, USA). As the ACSM was measuring continuously for a long time, the standard correction for instrument sensitivity drifts was applied to the dataset based on the inlet pressure and N_2 signal. Finally, mass concentrations were corrected using a Collection Efficiency (CE) to account for the particle bounce of aerosols on the vaporizer. The composition-dependent CE was calculated as described by Middlebrook et al. (2012) and was close to 0.45 for most of the time. Since for most ambient studies a 0.5 CE value is found to be representative with data uncertainties generally within ±20 % (Canagaratna et al., 2007), and since our ACSM concentrations using CE = 0.5 were in good agreement with concentrations from other co-located instruments, a CE of 0.5 was used.

The organic aerosol fraction was further investigated using Positive Matrix Factorization (PMF) (Paatero and Tapper, 1994) with the custom software tool of Source Finder (SoFi) version 4.7 developed by Canonaco et al. (2013), which enables evaluation of the PMF results together with statistical analysis. Only $m/z \leq 100$ were used for source apportionment of OA because: (a) the signals of $m/z > 100$ account for a minor fraction of the total organic mass (on average, 2 %), (b) the $m/z > 100$ have larger uncertainties, and (c) the large interference of naphthalene signals (used for m/z calibration of the ACSM) at these m/z (e.g., m/z 127, 128, and 129) (Sun et al., 2012).

2.3 Co-located measurements used in this study

MSC has been permanently equipped with aerosol monitoring instrumentation since January 2010 and some of these measurements were used in this study. 24 h PM_1

samples were collected every 4 days on 150 mm quartz micro-fiber filters (Pallflex QAT) using high volume samplers (30 $m^3 h^{-1}$, MCV CAV-A/MSb) equipped with MCV PM_1 cut-off inlets. Daily PM_1 mass concentrations were determined by off-line standard gravimetric procedures and chemical composition was obtained as described by Ripoll et al. (2014a) using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) and Mass Spectrometry (ICP-MS) for major and trace elements, respectively, Ion High Performance Liquid Chromatography (HPLC) and selective electrode for ions concentrations, and thermal-optical method for elemental carbons (EC) and organic carbon (OC) concentrations. Real-time PM_1 mass concentrations were continuously measured by an optical particle counter (OPC, Model GRIMM 1107). PM_1 30 min data were daily averaged and subsequently corrected by comparison with 24 h standard gravimetric mass measurements. The absorption coefficient was measured continuously using a Multi Angle Absorption Photometer (MAAP, model 5012, Thermo). Equivalent black carbon (BC) mass concentrations (Petzold et al., 2013) were calculated by the MAAP instrument software by dividing the measured absorption coefficient σ_{ap} (λ) by 6.6 $m^2 g^{-1}$, which is the mass absorption cross section (MAC) at 637 nm (Müller et al., 2011; Petzold and Schönlinner, 2004). Particle scattering (σ_{sp}; 0–360°) and hemispheric backscattering (σ_{bsp}; 90–270°) coefficients at three wavelengths (450, 525, 635 nm) were measured with a LED-based integrating nephelometer (model Aurora 3000, ECOTECH Pty, Ltd, Knoxfield, Australia). Finally, all meteorological data were measured by the Catalonian Meteorological Service from the Montsec d'Ares station. Gaseous pollutants (O_3, NO, NO_2, CO and SO_2) were measured using conventional real-time monitors belonging to the Department of Environment of the Autonomous Government of Catalonia.

In addition to these routine measurements, 2 intensive campaigns were performed in July–August 2011 and January–February 2012. During these intensive campaigns PM_1 filters were collected daily and a scanning mobility particle sizer (SMPS) was installed to measure particle number size distribution of diameters 11–350 nm in the summer campaign, and 8–450 nm in the winter campaign. The SMPS system comprises a differential mobility analyzer (DMA, Model TSI 3081) connected to a condensation particle counter (CPC, Model TSI 3772). The SMPS data for the winter campaign were also used to estimate the mass concentration to compare with the ACSM data. To this end, the volume size distributions were calculated from the measured particle number distributions assuming sphericity. The total volume concentrations were computed by integrating over the measured particle range and converted to mass concentration using the estimated composition-dependent density, calculated using the chemical composition given by the ACSM and the equation of Salcedo et al. (2006). Average concentrations shown in the whole paper are arithmetical averages unless otherwise specified.

2.4 Classification of meteorological episodes

The daily classification of meteorological episodes affecting MSC was made following the procedure described by Ripoll et al. (2014b), and the different air mass transport pathways determined were: Atlantic (AT), North African (NAF), Mediterranean (MED), European (EU), Winter Regional (WREG, from November to April), and Summer Regional (SREG, from May to October). The boundary layer height was calculated using the HYSPLIT model from the NOAA Air Resources Laboratory (http://www.ready.noaa.gov/READYamet.php) (Fig. S2).

3 Results and discussion

3.1 Submicron aerosol mass concentrations

In order to establish the consistency of the different measurements during this study, the sum of the ACSM species (= sulfate + nitrate + ammonium + OA + chloride) and the BC mass concentrations was compared with the co-located PM_1 and light scattering measurements (Fig. 1). The scatter plots of ACSM plus BC concentrations vs. PM_1

concentrations from the OPC and SMPS showed strong correlations ($R^2 = 0.72$ and $R^2 = 0.87$, respectively) and slopes close to unity (Fig. S3). Moreover, ACSM plus BC concentrations were also highly correlated with light scattering at 525 nm determined by the nephelometer ($R^2 = 0.85$, Fig. S3). The high degree of agreement is also apparent in the time series plots of PM_1 shown in Fig. 1.

The average concentration (25th, 50th, 75th percentiles) of the ACSM + BC mass during this study (July 2011–April 2012) was 4.9 µg m^{-3} (0.9, 2.8, 7.9 µg m^{-3}) (Table S1), which is similar to the 2010–2012 average reported by Ripoll et al. (2014b) from OPC measurements (5.0 µg m^{-3}). For the sake of brevity only summer and winter hourly variation will be discussed in the following sections, given that hourly variation in spring was similar to summer and that in fall was similar to winter. The seasonal average PM_1 concentrations were higher in summer (7.5 µg m^{-3} (3.4, 7.1, 10.5 µg m^{-3}), Table S1) than in winter (4.1 µg m^{-3} (0.8, 1.7, 5.6 µg m^{-3}), Table S1). A similar seasonal pattern has been described at other high altitude sites in Europe (e.g. Carbone et al., 2014; Cozic et al., 2008; Freney et al., 2011; Tositti et al., 2013), being associated with differences in the air mass origin from summer to winter, and also to variations in the planetary boundary layer (PBL) height. The seasonal variation at MSC has been described in detail in recent works (Pandolfi et al., 2014b; Ripoll et al., 2014a, b), and it has been principally attributed to the seasonal variation of the PBL (Fig. S2). In summer, the stable anticyclonic conditions over this continental area enhance convection increasing the development of the PBL and favoring the transport of anthropogenic pollutants towards high altitude sites such as MSC. The situation in winter is notably different, as the lower vertical development of the PBL over this area leaves high altitude sites in the FT, isolating MSC from polluted air masses. The seasonal variation of PM concentrations at MSC has been also connected to mesoscale and synoptic meteorological processes. At MSC, southern flows and regional recirculation episodes are more frequent in summer, whereas clean Atlantic advections and northeastern winds from mainland Europe are more common in winter (Fig. S4 and Table S2) (Pandolfi et al., 2014b; Ripoll et al., 2014a, b).

3.2 Submicron aerosol chemical composition

Concentrations of ACSM species were daily averaged and compared with off-line measurements from 24 h PM_1 samples, and all species showed strong correlations (R^2 between 0.77 and 0.96, Fig. S5). Different slopes (ACSM vs. off-line measurements) were found for each of the species: 1.12 for sulfate, 1.31 for ammonium and 1.35 for nitrate. The relatively higher slope for nitrate, with respect to sulfate, can be attributed to a sampling negative artifact due to the volatilization of nitrate on the off-line samples (Schaap et al., 2004). Ammonium is present as a counterion for sulfate and nitrate, and thus its slope is in between those of the two species.

For the OA, the slope could be interpreted as the OM-to-OC ratio, since the off-line measurements determined organic carbon. This slope was found to be 3.39, however values of 2.2 are more common for aged aerosol (e.g. Aiken et al., 2008; Minguillón et al., 2011; Takahama et al., 2011). This disagreement of a factor of 1.54 may be attributed to different reasons. A negative volatilization artifact may occur in the filters, hence resulting in an underestimation of OC. Alternatively it is possible that the RIE for OA in the ACSM is larger than the value of 1.4 determined for the AMS, a topic currently being investigated by the ACSM manufacturer, which would result in an overestimation of OA. Similar series of intercomparisons with a similar discrepancy for OA has been found for a one-year dataset with the same instrument at another site (unpublished data) and for a recently reported study in Atlanta, US by Budisulistiorini et al. (2014). Assuming that the disagreement was due to the overestimation by the ACSM, the OA concentrations were corrected dividing by the disagreement factor (1.54) to compare the results with co-located measurements (Fig. S3). The resulting slopes were within the uncertainties and hence OA concentrations reported in the present paper were not corrected since further research is needed to better estimate the RIE for OA in the ACSM.

The average of PM_1 chemical composition at MSC during this study (July 2011–April 2012) is given in Fig. 2. On average, OA was the largest PM_1 constituent (50 %), followed by sulfate (20 %), nitrate (14 %), ammonium (12 %), BC (4 %) and chloride (1 %). As was the case of PM_1 concentrations, all chemical components increased in summer and decreased in winter, with the exception of nitrate (Fig. 2 and Table S1). The higher nitrate concentrations in winter than in summer were also observed in other studies in the Mediterranean region (e.g. Pey et al., 2009; Querol et al., 2009; Ripoll et al., 2014a) and this variation was attributed to the high volatility of ammonium nitrate at low humidity and high temperature (Zhuang et al., 1999). At MSC, the summer maximum of the rest of PM components has been mainly ascribed to the higher temperature and solar radiation in summer (Table S2), which enhances atmospheric photochemistry, promoting the formation of secondary inorganic and organic aerosols. All these seasonal characteristics are described in detail in Ripoll et al. (2014a).

3.2.1 Summer trends

Time series of PM_1 components during summer time (14 July–24 September 2011) are shown in Fig. 3. Wind direction and wind speed, temperature, precipitation and concentrations of nitrogen oxides, sulfur dioxide, and ozone are also depicted. The daily classification of meteorological episodes affecting MSC is also illustrated in different background colors. On average, during summer the lowest concentrations of all PM_1 components and gases were recorded under the Atlantic advection conditions since these air masses are associated with precipitation, decreased temperature and solar radiation, and strong winds, leading to cleaner atmospheric conditions. Conversely, summer regional episodes lasted for 6 to 11 consecutive days and led to sustained increases of the background concentrations of sulfate, OA and BC at MSC. Despite the limited ACSM data availability during North African episodes, relatively high concentrations of PM_1 components were observed under this type of episodes, especially BC (Fig. 3).

The diurnal cycles of PM_1 components, gaseous pollutants and meteorological variables are shown in Fig. 4. The summer concentrations of PM_1 components and gases showed no clear diurnal patterns, except for ozone and OA. This lack of defined daily patterns is similar to the findings obtained at the high altitude Puy-de-Dôme station in central France (Freney et al., 2011, the only similar study found at a remote site). For a high altitude site as MSC, the lack of diurnal cycles can be explained by a combination of factors. In summer, the recirculation of air masses over the WMB induced by an abrupt orography (Fig. S1) causes the formation of reserve pollution strata at any time at relatively high altitudes (Millan et al., 1997; Rodríguez et al., 2003). Moreover, long-range transport from North Africa, which can be more intense at high altitude layers (Ripoll et al., 2014a), could also blur the daily patterns since the occurrence of this transport does not depend on the time of the day. These factors result in a lack of well-defined daily patterns but in a high variability of diurnal cycles even within the same type of episode, which is reflected in the similar average daily evolutions and the high SDs calculated for the average daily patterns when separated by air mass origin (Fig. S6).

The ozone and OA concentrations had a marked diurnal cycle regardless of the air mass origin (Figs. 4 and S6) in summer. These different daily patterns with respect to the rest of the gases and chemical components points to the fact that ozone and OA variations are strongly influenced by local/regional processes and not just dominated by long-range transport. Minimum ozone concentrations were recorded between 08:00 and 09:00 UTC, whereas maximum concentrations were measured between 16:00 and 17:00 UTC. In contrast, the highest OA concentrations were observed around 12:00 UTC, and the lowest during the night and in the early morning. The ozone variations may influence those of OA, although the complete understanding of the ozone diurnal evolution is outside the scope of this study. The average increase in OA during the day is likely due to the photooxidation of volatile organic compounds (VOCs). Given that MSC is a remote site, in summer VOCs are most likely dominated by local biogenic emissions (BVOCs), as it was found in the Mediterranean forested area of Montseny (Seco et al., 2011). Hence, the midday increase is likely due to recently-produced biogenic SOA, and to a lesser degree, photooxidation of anthropogenic VOCs.

Despite the marked diurnal cycle of OA regardless of air mass origin, the average increase during the day with respect to average concentrations during the night was higher under summer regional ($2.6\,\mu g\,m^{-3}$) and North African ($3.0\,\mu g\,m^{-3}$) episodes than during Atlantic advections ($1.3\,\mu g\,m^{-3}$) (Fig. S6). This difference could be caused by the higher SOA formation. This is due to the increase in BVOCs emissions and atmospheric photooxidation caused by the higher temperature and solar radiation (Paasonen et al., 2013; Seco et al., 2011) under summer regional and North African episodes. Furthermore, under these episodes higher concentrations of ozone were measured, which also favors the formation of SOA (via direct oxidation and also by leading to higher OH concentrations). The SOA formation registered at MSC is relatively high when compared to other high altitude sites such as Puy-de-Dôme (Freney et al., 2011). This is in agreement with the modeled SOA emissions in different areas, which identified higher SOA concentrations in Mediterranean environments (Bessagnet et al., 2008). This higher SOA formation is probably due to the higher emissions of BVOCs in the Mediterranean forested areas (up to 3 times higher than Boral areas) (Bessagnet et al., 2008; Lang-Yona et al., 2010; Steinbrecher et al., 2009) and the comparable concentrations of tropospheric ozone with other high altitude European sites (Chevalier et al., 2007). On the other hand, the extra formation of SOA under summer regional and North African episodes might also have a contribution from the photooxidation of anthropogenic VOCs, since Atlantic advections are associated with cleaner atmospheric conditions.

3.2.2 Winter trends

As was the case during summer, in winter the lowest concentrations of all PM_1 components and gases were recorded under the Atlantic advections, whereas the highest were measured when MSC was affected by air masses from mainland Europe and sporadically under regional conditions (Fig. 5). Mediterranean air masses were detected very infrequently and therefore conclusions on their characteristics will not be drawn in the present paper. The relative contribution of different components was similar, with OA representing a somewhat smaller fraction than in summer.

In contrast to what was found in summer, in winter concentrations of most PM_1 components and gaseous pollutants showed much clearer diurnal patterns, with a minimum around 07:00 UTC and a maximum between 14:00 and 15:00 UTC (Fig. 4). Similar patterns have been observed at the Puy-de-Dôme station during a winter campaign (Freney et al., 2011). These daily cycles are probably caused by the fact that MSC is located most of the day within the FT in winter, whereas PBL air masses are only injected upwards after midday (Fig. S2). Moreover, thermal inversions are very frequent from 20:00 to 07:00 UTC. These situations prevent the transport of pollutants from the lower populated areas towards higher altitudes, especially at night. During the morning, the thermal inversions dissipate due to the radiative warming of the ground and mountain upslope winds develop. These mountain winds transport anthropogenic and biogenic emissions from the adjacent valleys and plains to the top of the mountain, with a maximum upslope transport in the afternoon. Thus, mountain breezes play an important role in determining the diurnal variation of PM_1 components in winter (Fig. 4), especially under regional conditions. A clear example of the PM_1 components diurnal pattern under winter regional episodes was observed from 22 to 25 February 2012 with PM_1 concentrations (and NO_x) increasing several fold during the afternoon (Fig. 5).

In contrast, the study of the daily cycles as a function of air mass origin (Fig. S7) showed less marked daily patterns when MSC is affected by Atlantic advections and long-range transport from mainland Europe, since in both cases long-range advection play a more important role. Under Atlantic episodes the concentrations of PM_1 components were very low and the SDs with respect to the average pattern were quite high, resulting in unclear diurnal patterns. On the other hand, under European episodes, which can be more intense at high altitude layers (Ripoll et al., 2014a; Sicard et al., 2011), background concentrations of PM_1 components were higher and the midday increment was lower, resulting in less marked daily patterns. These less-marked diurnal cycles are probably due to the fact that the increase of PM_1 components occurs during these episodes regardless of the time of the day. A good example of this less-marked hourly variation during European episodes was observed from 17 to 19 February 2012 (Fig. 5).

3.3 Characterization of OA components

The PMF analysis was applied to the dataset from the whole period and to the summer and winter periods separately, and the results obtained from each analysis were comparable, with strong correlations between corresponding component profiles (Fig. S8). The solution selected from the PMF analysis was based on the mass spectra, time series of each factor compared to external tracers (including nitrate, sulfate, BC and ozone) and daily patterns of each factor. As a result, two different types of oxygenated organic aerosol (OOA) were resolved: semi-volatile oxygenated organic aerosol (SV-OOA) and low-volatile oxygenated organic aerosol (LV-OOA). The SV-OOA was characterized by dominant mass spectral peaks at m/z 43, 44 and 55, and the LV-OOA was defined by having dominant peaks at m/z 44 and 41 (Fig. 6). The one substantial difference in the factor profiles using different periods was that the LV-OOA resolved using the whole measurement period has about double the m/z 44 contribution compared to winter suggesting that LV-OOA is generally more oxidized during the summer. No other organic components could be identified by the PMF analysis probably because primary organic emissions are mixed and oxidized during their transport from industrial and urban areas to the remote site of MSC. This is in agreement with what was found in other remote sites (Freney et al., 2011; Raatikainen et al., 2010) and confirms the initial hypothesis of MSC organic components being mostly from SOA, as previous studies showed that OOA is mainly secondary in their origin (e.g. Jimenez et al., 2009; Ng et al., 2011a; Zhang et al., 2007). Furthermore, the origin of OA has been recently investigated in the Mediterranean forested area of Montseny, and it has been found that SOA accounted for 91 % (Minguillón et al., 2011). That study identified a contribution from biomass burning (including both primary and secondary OC) of 22 % of the total OC at Montseny, however, at MSC biomass burning organic aerosol (BBOA) could not be separately identified, perhaps due to its aging into OOA-like components (Cubison et al., 2011). The PMF results discussed below correspond to PMF analysis applied to the whole period.

On average, SV-OOA dominated the OA fraction, but its contribution decreased from 72 % in summer to 61 % in winter, whereas LV-OOA contributed 28 % in summer vs. 39 % in winter (Figs. 7 and 8). SV-OOA has been previously described as the less oxygenated and semi-volatile fraction of OOA (Ng et al., 2011a) and therefore it has been mostly attributed to SOA formation from more local emissions (Jimenez et al., 2009). Conversely, the LV-OOA has been generally associated with highly oxidized, aged, and long-range-transported aerosol particles (Lanz et al., 2010). Hence, at MSC the local or regional emissions of SOA precursors result in a higher contribution to total SOA than the long-range-transported SOA, especially in summer.

The diurnal cycles of OA components were studied as a function of air mass origin (Figs. 7 and 8). As for the case of total organic concentrations, hourly variations of SV-OOA and LV-OOA concentrations showed a clear daily pattern regardless of the air mass origin, especially the SV-OOA concentrations, and except for AT advections in winter. In summer, the maximum concentrations of SV-OOA and LV-OOA were measured between 11:00 and 12:00 UTC, whereas those in winter were observed around 14:00 UTC. Moreover, the midday increase with respect to night average concentrations of SV-OOA concentrations varied from 0.9 to 2.1 $\mu g\,m^{-3}$ in summer and from 0.3 to 2.2 $\mu g\,m^{-3}$ in winter, whereas LV-OOA increase ranged from 0.4 to 0.8 in summer and from 0.4 to 1.0 $\mu g\,m^{-3}$ in winter. The higher increase in SV-OOA with respect to that of LV-OOA further confirms the more local or regional origin of SV-OOA and the more background character of the LV-OOA. The seasonal variations can be attributed to the higher production of SOA in summer as opposed to winter, when the maximum daily concentrations are reached later driven by the mountain breezes.

4 Conclusions

This work interprets the real-time variation of inorganic and organic submicron components during 10 months (July 2011–April 2012) at a high altitude site in southern Europe (Montsec, 1570 m a.s.l.). The aerosol chemical composition was obtained with an Aerosol Chemical Speciation Monitor, and co-located on-line and off-line PM_1 measurements were also carried out to complement the ACSM dataset. The average concentration of the ACSM plus BC mass during this study was 4.9 µg m^{-3}, and on average OA was the foremost PM_1 constituent (50 %), followed by sulfate (20 %), nitrate (14 %), ammonium (12 %), BC (4 %) and chloride (1 %). Discrepancies of OA determined by ACSM with co-located measurements pointed to an overestimation by the ACSM probably caused by the use of the default RIE for OA, which could be lower than the actual one.

The seasonal variation of PM_1 mass and chemical components concentrations showed similar patterns, with an increase in summer and a decrease in winter, except for nitrate which has high volatility in summer. The seasonal variation was attributed to the evolution of the PBL height throughout the year and to synoptic circulation and meteorological factors. At MSC the higher temperature and solar radiation in summer enhances the convection processes, incrementing the development of the PBL, and augments atmospheric photochemistry, promoting the formation of secondary inorganic and organic aerosols.

The diurnal variation of PM_1 components had no clear diurnal patterns in summer, except for organics. This lack of defined daily patterns was ascribed to the recirculation of air masses that causes the formation of reserve strata at relatively high altitudes, and to the long-range transport from North Africa. These factors result in a high variability of diurnal cycles even within the same type of episode. Nevertheless, organic concentrations had a marked diurnal cycle regardless of the air mass origin, with maximum concentrations around 12:00 UTC. This midday increase with respect to average concentrations during the night was attributed to the formation of SOA.

In winter under regional conditions, concentrations of all PM_1 components showed much clearer diurnal patterns than in summer, with a maximum between 14:00 and 15:00 UTC. These daily cycles were connected to the fact that MSC is located most of the day within the FT, whereas PBL air masses are only injected upwards after midday. However, when MSC was affected by long-range transport from mainland Europe, less marked daily patterns of PM_1 components were observed.

In order to characterize the different organic aerosol components existing at MSC, the organic fraction from the ACSM mass spectra was investigated using PMF analysis. As a result, two different types of oxygenated organic aerosol (OOA) were determined: semi-volatile oxygenated organic aerosol (SV-OOA) and low-volatile oxygenated organic aerosol (LV-OOA). On average, the SV-OOA dominated the OA fraction, but its contribution decreased from 72 % in summer to 61 % in winter, whereas the LV-OOA contribution varied from 28 % in summer to 39 % in winter. The hourly variation of SV-OOA and LV-OOA concentrations showed a clear diurnal pattern throughout the year regardless of the air mass origin.

To the authors' knowledge, this is one of the first times when real-time submicron aerosol chemical composition is characterized and its variation is interpreted during almost a year in a continental background environment. The results obtained in the present study highlight the importance of the SOA formation processes at such remote site as MSC, which could be the objective of further investigations.

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Title Page
Abstract Introduction
Conclusions References
Tables Figures
◀| |▶
◀ ▶
Back Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

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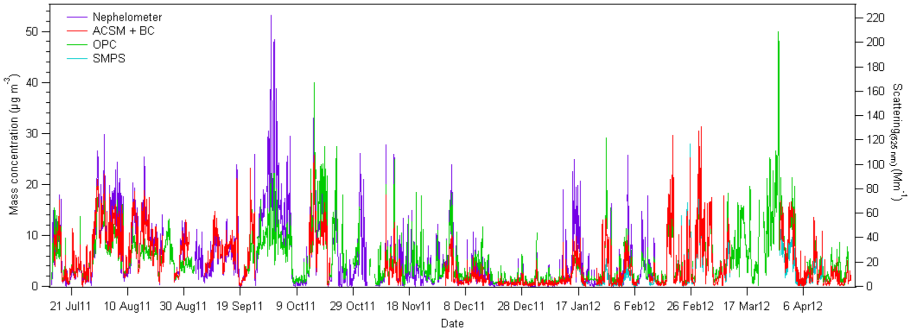

Figure 1. Time series of PM_1 total mass from co-located measurements and light scattering at 525 nm.

Title Page
Abstract | Introduction
Conclusions | References
Tables | Figures
◀| |▶
◀ ▶
Back | Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

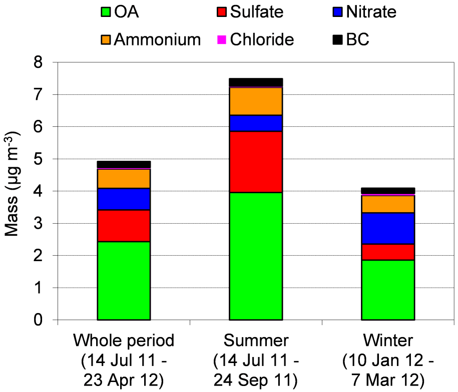

Figure 2. Average concentrations of PM_1 chemical species measured at Montsec during the study.

Figure 3. Time series of wind direction, precipitation, temperature, wind speed, concentrations of nitrogen oxides (NO_x), sulfur dioxide (SO_2), ozone (O_3), and PM_1 chemical species (OA, sulfate, nitrate, ammonium, chloride and black carbon (BC)) in summer (14 July 2011–24 September 2011). Background colors correspond to daily classification of meteorological episodes (summer regional (SREG), North African (NAF), Atlantic (AT)) and the pie chart correspond to the average chemical composition for the summer period.

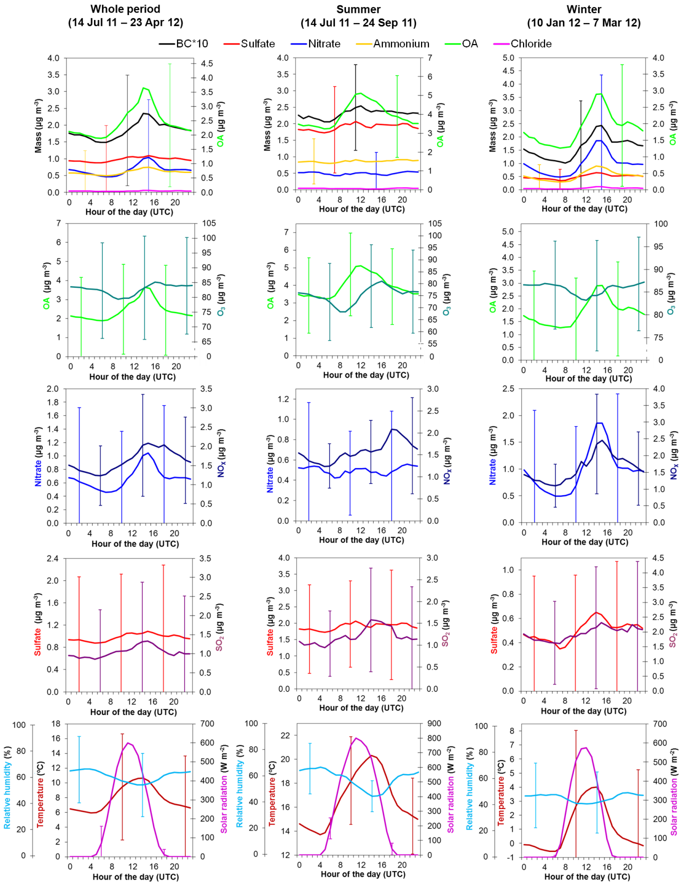

Figure 4. Diurnal cycles of PM_1 chemical species (black carbon (BC), sulfate, nitrate, ammonium, chloride and OA), gaseous pollutants (ozone (O_3), nitrogen oxides (NO_x), and sulfur dioxide (SO_2)), and meteorological parameters (relative humidity, temperature and solar radiation) averaged for the whole period, summer and winter. Variation bars indicate ±SD.

Title Page
Abstract Introduction
Conclusions References
Tables Figures
|◀ ▶|
◀ ▶
Back Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

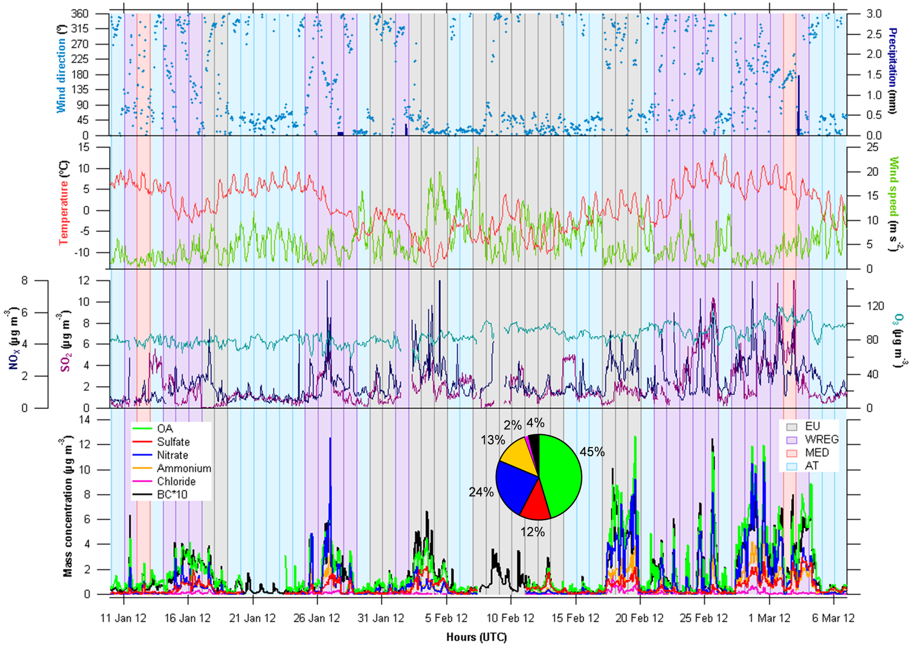

Figure 5. Time series of wind direction (WD) and speed (WS), temperature (T), precipitation (PP), concentrations of nitrogen oxides (NO_x), sulfur dioxide (SO_2), ozone (O_3), and PM_1 chemical species (organics, sulfate, nitrate, ammonium, chloride and black carbon (BC)) in winter (10 January 2012–7 March 2012). Background colors correspond to daily classification of meteorological episodes and the pie chart correspond to the average chemical composition for the winter period.

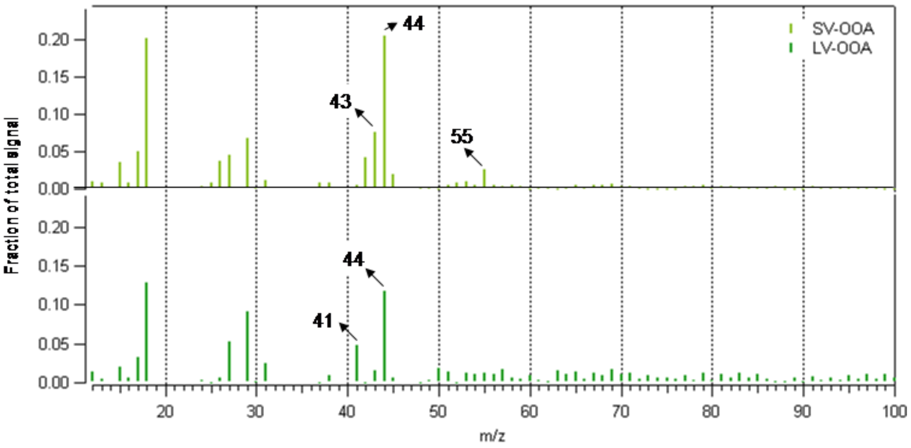

Figure 6. Organic species (Semi-Volatile Oxygenated Organic Aerosol (SV-OOA) and Low-Volatility Oxygenated Organic Aerosol (LV-OOA)) profiles extracted from the PMF analysis for the whole period (14 July 2011–23 April 2012).

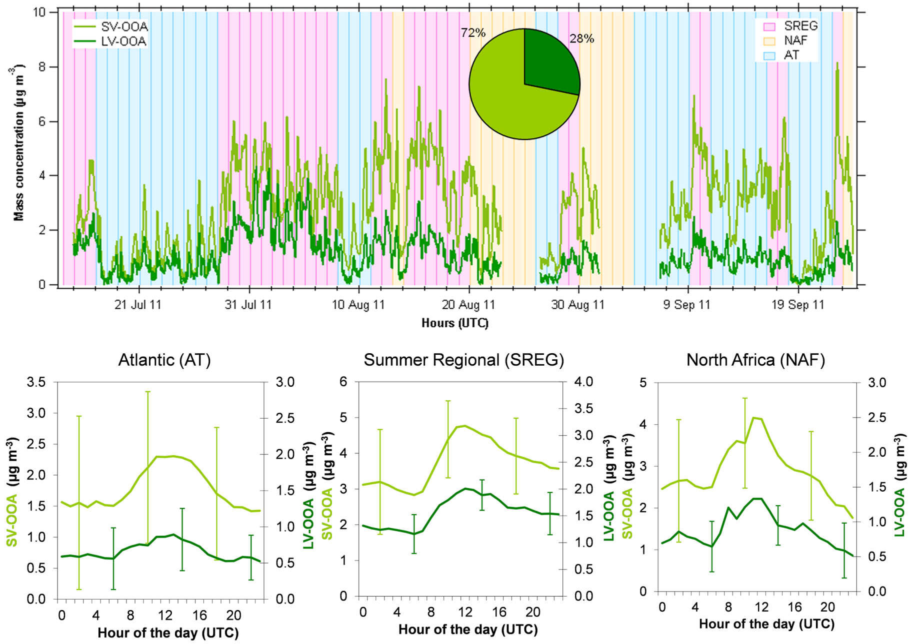

Figure 7. Top: time series of organic species (Semi-Volatile Oxygenated Organic Aerosol (SV-OOA) and Low-Volatility Oxygenated Organic Aerosol (LV-OOA)) concentrations in summer (14 July 2011–24 September 2011). Background colors correspond to daily classification of meteorological episodes and the pie chart correspond to the average organic species composition for the summer period. Bottom: diurnal cycles of organic species concentrations averaged as a function of meteorological episode for the summer period. Variation bars indicate ±SD.

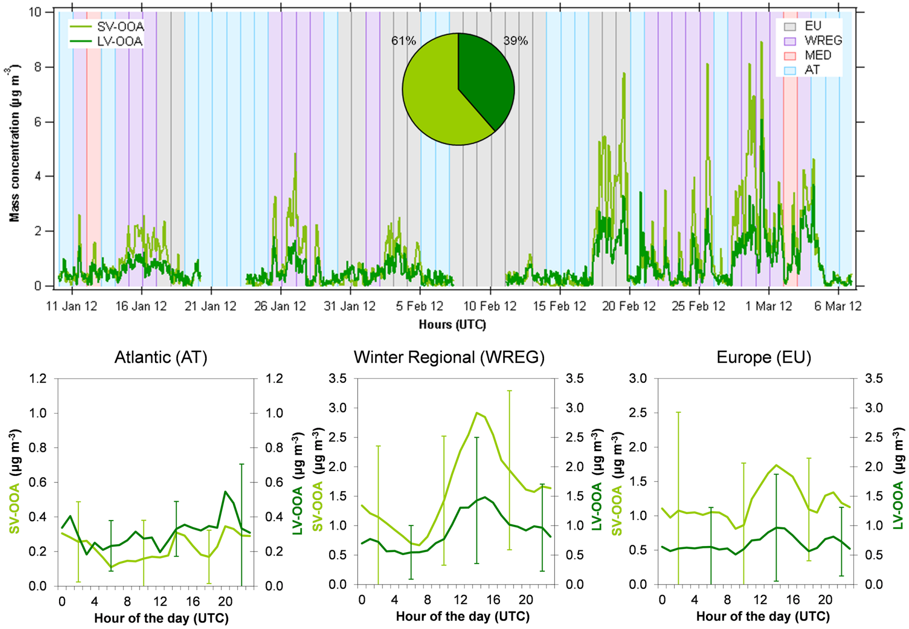

Figure 8. Top: time series of organic species (Low-Volatility Oxygenated Organic Aerosol (LV-OOA) and Semi-Volatile Oxygenated Organic Aerosol (SV-OOA)) concentrations in winter (10 January 2012–7 March 2012). Background colors correspond to daily classification of meteorological episodes and the pie chart correspond to the average organic species composition for the winter period. Bottom: diurnal cycles of organic species concentrations averaged as a function of meteorological episode for the winter period. Variation bars indicate ±SD.