Joint analysis of continental and regional background environments in the Western Mediterranean: PM_1 and PM_{10} concentrations and composition

A. Ripoll[1,2]*, M. C. Minguillón[1], J. Pey[1,3], N. Pérez[1], X. Querol[1], 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 Franquès 1, 08028, Barcelona, Spain

[3]Now at: Aix-Marseille Université, CNRS, LCE FRE 3416, Marseille, 13331, France

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

Abstract. The complete chemical composition of atmospheric particulate matter (PM_1 and PM_{10}) from a continental (Montsec, MSC, 1570 m a.s.l.) and a regional (Montseny, MSY, 720 m a.s.l) background site in the Western Mediterranean Basin (WMB) were jointly studied for the first time for a relatively long-term period (January 2010-March 2013).

Differences in average PM_X concentration and composition between both sites were attributed to: distance to anthropogenic sources, altitude, and different influence of atmospheric episodes. All these factors result in a continental to regional background increase of 4.0 μg m^{-3} for PM_{10} and 1.1 μg m^{-3} for PM_1 in the WMB. This increase is mainly constituted by organic matter, sulfate, nitrate and sea salt. However, higher mineral matter concentrations were measured at the continental background site owing to the higher influence of long-range transport of dust and dust resuspension.

Seasonal variations of aerosol chemical components were ascribed to: evolution of the planetary boundary layer (PBL) height throughout the year, variations in the air mass origin, and differences in meteorology. During warmer months, weak pressure gradients and elevated insolation generate recirculation of air masses and enhances the development of the PBL, causing the aging of aerosols and incrementing pollutant concentrations over a large area in the WMB, including the continental background. This is reflected in a more similar relative composition and absolute concentrations of continental and regional background aerosols. Nevertheless, during colder months the thermal inversions and the lower vertical development of the PBL leave MSC in the free troposphere most of the time, whereas MSY is more influenced by regional pollutants accumulated under winter anticyclonic conditions. This results in much lower concentrations of PM_X components at the continental background site with respect to those at the regional background site.

The influence of certain atmospheric episodes caused different impacts at regional and continental scales. When long-range transport from Central and Eastern Europe and from North Africa occurs, the continental background site is frequently more influenced, thus indicating a preferential transport of pollutants at high altitude layers. Conversely, the regional background site was more influenced by regional processes.

Continental and regional aerosol chemical composition from the WMB revealed: a) high relevance of African dust transport and regional dust resuspension; b) low biomass burning contribution; c) high organic matter contribution; d) low summer nitrate concentrations; and e) high aerosol homogenization in summer.

Keywords: remote, high altitude, mountain, tropospheric aerosols, rural.

1 Introduction

The influence of atmospheric particulate matter (PM) on the Earth's radiative budget generates a strong scientific interest because of its effect on climate. Atmospheric PM interacts with the Earth's climate system by scattering and absorbing solar radiation (direct climate forcing effect), and by acting as cloud condensation nuclei (indirect climate forcing effect) (IPCC, 2013). Aerosols also have adverse effects on air quality (Directive 2008/50/EC) and human health (WHO, 2013), as well as on ecosystems (e.g. Burkhardt and Pariyar, 2014). The size distribution of aerosol chemical components is a key factor in modulating these effects, and provides valuable information on the aerosol origins and sources. Aerosol chemical composition measurements carried out at complex sites such as urban areas constrain the assessment of the origin of regional and long-range transported aerosols, as local sources prevail. For this reason, measurements performed at a sufficient distance from large emission sources are needed to determine background conditions and to evaluate air mass transport effects. Furthermore, an improved understanding of synoptic and mesoscale meteorological effects is necessary to develop a better predictive capability of air quality and climate models.

Although there is not a well-established definition, continental background environments can be described as representative of the air quality of a wide area of hundreds of kilometers, as proposed by Laj et al. (2009), with the absence of local emissions. However, aerosols found in this type of environments are not purely natural, the presence of some pollutants in these sites indicates that they are affected by long-range transport of anthropogenic emissions, since generally they are isolated from large polluted areas (>50 km)

(Putaud et al., 2010). For this reason, these environments are also classified as remote sites. In many cases the monitoring sites chosen to represent this type of environments are located in mountaintops over 1000 m above sea level (a.s.l.), therefore they are also called high altitude sites (Nyeki et al., 1998) or free troposphere (FT) environments (Andrews et al., 2011). The areas located at sufficient distance from large anthropogenic sources but frequently within the planetary boundary (PBL) are classified as regional background environments (Putaud et al., 2010). These environments are representative of the air quality of a less extensive area and they are more influenced by regional transport of polluted air masses than continental background environments.

Aerosol chemical characterization has been performed at many locations across Europe, providing information on PM_{10} and $PM_{2.5}$ chemical composition from different types of environments (e.g. Putaud et al., 2010), improving the knowledge on the variation and trends of PM composition (e.g. Cusack et al., 2012), and increasing the understanding of PM sources (Belis et al., 2013). Nevertheless, the PM_1 fraction remains relatively understudied, especially outside urban areas. Most studies focusing on PM_1 have been carried out within the PBL whereas measurements at continental background sites in Europe are scarce and they were mostly taken in short-term measurement campaigns (e.g. Carbone et al., 2010; Marenco et al., 2006). The study of PM_1 chemical composition at continental background sites may be necessary to assess the contribution of regional and long-range transport, since it is in the PM_1 fraction where most of the anthropogenic constituents are concentrated (Minguillón et al., 2012; Pérez et al., 2008b).

Among the few long-term European studies at continental background environments, Cozic et al. (2008) investigated the chemical composition of coarse and PM_1 aerosols for 7 years at the high alpine site of Jungfraujoch (Switzerland). Bourcier et al. (2012) studied PM_{10} and PM_1 water-soluble inorganic components over one year at the high altitude site of Puy de Dôme (France). Recently, Carbone et al. (2014) performed a study on long-term measurements of chemical composition in the continental background environment of the Southern Europe/Northern Mediterranean. This study was focused on nocturnal PM_1 chemical composition for 3 years at the high mountain station of Mt. Cimone (Italy).

The Mediterranean region 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 (Pey et al., 2010, 2013b; Ripoll et al., 2014), and accumulation and recirculation processes are recurrently observed (Rodriguez et al., 2002).

For these reasons, results of PM_{10} and PM_1 chemical characterization from Montsec (MSC) and Montseny (MSY) Global Atmosphere Watch (GAW) stations for the period of January 2010-March 2013 are presented in this study. MSC is representative of the continental background conditions of the Western Mediterranean Basin (WMB) (Ripoll et al. 2014). This station is located in the FT most of the time due to its elevation (1570 m a.s.l.); although during the warmer months that isolation is broken as a result of vertical mixing and mountain breeze regimes (Ripoll et al. 2014). MSY is a regional background observatory located in the WMB (720 m a.s.l.) in operation since 2002 (Cusack et al., 2012; Pérez et al., 2008a) and it is influenced by regional anthropogenic emissions in specific scenarios (Pérez et al., 2008a; Pey et al., 2010). The record of a relatively long series of PM_{10} and PM_1 concentrations and complete chemical composition at two different WMB environments has allowed for the investigation of temporal and spatial aerosol variations in the WMB with focus on regional and long-range transport processes. Daily and seasonal patterns of PM_{10} and PM_1 concentrations, as well as their major components and trace elements at MSC and MSY, were investigated. Greater emphasis was placed on the evaluation of the influence of different meteorological scenarios, with a focus on the partitioning of the chemical components into different size fractions in order to discriminate natural and anthropogenic impacts affecting PM_{10} and PM_1. To the authors' knowledge, no similar studies exist in the literature which compares continental and regional background environments and their seasonal variation.

2 Methodology

2.1 Monitoring sites and sampling schedule

The continental background site was set up in the Montsec (MSC) mountain range, located in the NE of the Iberian Peninsula (42º3'N, 0º44'E, 1570 m a.s.l.). This station is situated at 50 km to the S of the Axial Pyrenees and at 140 km to the NW of Barcelona (Fig. S1). A detailed description of this site can be found in Ripoll et al. (2014).

Results from MSC were jointly studied with those simultaneously obtained at the Montseny (MSY) station, a regional background observatory located in the Montseny Natural Park (41º19'N, 02º21'E, 720 m a.s.l.), 40 km to the N-NE of the Barcelona urban area, and 25 km from the Mediterranean coast (Fig. S1) (Pérez et al., 2008a).

At MSC site, 24-h samples of PM_{10} and PM_1 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_{10} and PM_1 cut-off inlets. PM_{10} and PM_1 sampling began in November 2009 and in March 2011, respectively. In this work we study the results from January 2010 (March 2011 for PM_1) to March 2013. In addition to the routine measurements, 5 intensive campaigns (daily sampling) were performed during Mar-Apr 2011, Jul-Aug 2011, Jan-Feb 2012, Jun-Jul 2012 and Jan-Feb 2013. Overall, 391 and 235 samples of PM_{10} and PM_1, respectively, were collected throughout the study period, and PM_{1-10} concentrations were calculated by the difference of simultaneous PM_1 and PM_{10} daily samples (190 days).

At MSY site, 24-h samples of PM_{10} and PM_1 were also collected from January 2010 to March 2013 using high volume samplers (30 m^3 h^{-1}, DIGITEL-DH80) equipped with PM_{10} and PM_1 cut-off inlet (also DIGITEL). A total of 351 and 335 samples of PM_{10} and PM_1, respectively, were collected during the study period, and PM_{1-10} samples were calculated for 147 days. In most cases, sampling days were coincident at MSC and at MSY.

173 *2.2 Chemical characterization*

174 PM mass concentrations were determined by standard gravimetric
175 procedures, and complete chemical analysis for all filters was performed
176 following the procedures proposed by Querol et al. (2001).

177 Acid digestion ($HF:HNO_3:HClO_4$) of 1/4 of each filter was carried out to
178 determine and quantify major and trace elements by Inductively Coupled
179 Plasma Mass Spectrometry (ICP-MS, X Series II, THERMO) and Atomic
180 Emission Spectroscopy (ICP-AES, IRIS Advantage TJA solutions, THERMO).
181 Few mg of the reference material NIST 1633b were added to 1/4 of laboratory
182 blank filters to check the accuracy of the analysis of the acidic digestions. One
183 1/4 of each filter was leached with ultrapure water (miliQ) to determine the
184 content of Cl^-, SO_4^{2-}, and NO_3^- by Ion High Performance Liquid Chromatography
185 (HPLC) using a WATERS ICpakTM anion column with a WATERS 432
186 conductivity detector, and NH_4^+ concentrations with a Selective Electrode
187 (MODEL 710 A+, THERMO Orion). A rectangular portion (1.5 cm^{-2}) of the
188 remaining filter was used for the analysis of organic carbon (OC) and elemental
189 carbon (EC) by a SUNSET OCEC analyzer using the EUSAAR 2 protocol
190 (Cavalli et al., 2010). Moreover, one blank filter was kept for each set of ten
191 filters. Blank concentrations were subtracted from the total concentration
192 measured for each sample, thus giving ambient concentrations. To complete
193 mass balances, the following indirect determinations were obtained: a) CO_3^{2-},
194 calculated from Ca as $CO_3^{2-}=1.5*Ca$; b) Al_2O_3, calculated from Al as
195 $Al_2O_3=1.889*Al$; c) SiO_2, calculated as $SiO_2=2.5*Al_2O_3$, and d) organic matter
196 (OM) obtained applying a 2.2 factor to the OC concentrations for MSC samples
197 and a 2.1 factor for MSY samples, following the suggestion from Takahama et
198 al. (2011). By following these procedures we were able to determine and
199 quantify the concentrations of major components (OC, EC, SiO_2, CO_3^{2-}, Al_2O_3,
200 Ca, Al, Na, Mg, Fe, K, NO_3^-, SO_4^{2-}, NH_4^+ and Cl^-) and trace elements (Li, P, Ti,
201 V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Rb, Sr, Cd, Sn, Sb, Ba, La, Pb, among
202 others). Overall, the aforementioned components accounted for 60–90% of the
203 total PM mass. Most of the undetermined mass was attributed to water not
204 eliminated during filter conditioning in the presence of hygroscopic species, but
205 a contribution from sampling artifacts and from the use of factors to determine
206 CO_3^{2-}, SiO_2, and OM cannot be discarded.

At MSC the mineral matter (MM) determination was calculated as:

$$MM=CO_3^{2-}+SiO_2+Al_2O_3+Ca+Fe+K+nss\text{-}Na+Mg+Mn+Ti+P \quad [1]$$

Where nss-Na is the non-sea-salt sodium and it was calculated as nss-$Na=Al_2O_3*0.067$ according to the composition of the mineral particles from the Sahara given by Moreno et al. (2006), and hence the remaining sodium was sea-salt sodium (ss-Na=Na - nss-Na).

Consequently, the sea salt (SS) determination at MSC was given by:

$$SS=Cl^- + ss\text{-}Na \quad [2]$$

At MSY, Na concentrations were totally attributed to SS, given that it is located closer to the sea and in agreement with Pey et al. (2009).

2.3 Principal component analysis

Principal component analysis (PCA) was performed using the software STATISTICA v10.0. The orthogonal transformation method with Varimax rotation (Thurston and Spengler, 1985) was employed, retaining principal components with eigenvalues greater than one. The dataset used for PCA was comprised of the following PM_{10} constituents Cl^-, NO_3^-, NH_4^+, SO_4^{2-}, Al_2O_3, Ca, K, Na, Mg, Fe, Li, Ti, V, Cr, Mn, Ni, Cu, Zn, As, Se, Sr, Cd, Sb, Pb, OC and EC. All days with measurements of PM_{10} chemical analysis were included for PCA analysis, which totalled 390 cases from MSC and 351 cases from MSY. A typical robust PCA analysis requires at least a dataset with 100 cases. This technique allowed for the identification of main common groups of trace elements in PM_{10} at the continental and regional background sites.

2.4 Classification of atmospheric episodes

The classification of the atmospheric episodes affecting MSC and MSY sites on each day of the sampling period was performed following the procedure described by Ripoll et al. (2014), and the different air mass transport pathways determined were: 1) Atlantic North (AN), 2) Atlantic North West (ANW), 3) Atlantic South West (ASW), 4) North Africa (NAF), 5) Mediterranean (MED), 6) Europe (EU), 7) Winter Regional (WREG, from November to April), and 8) Summer Regional (SREG, from May to October) (Fig. 1).

Additionally, the boundary layer height was calculated at MSC and MSY sites using the READY model from the NOAA Air Resources Laboratory

(http://www.ready.noaa.gov/READYamet.php), which is based in meteorological conditions defining Pasquill stability classes, and uses a resolution grid of 50 km. This was calculated every three hours during the whole period (Fig. S2). Despite the limited suitability of this type of model for mountainous terrains, the differences found throughout the year and among different atmospheric scenarios can be considered as a good approximation of the actual PBL variations.

3 Results and discussion

3.1 Continental vs. regional background PM concentrations in the Western Mediterranean

PM_{10} and PM_1 average concentrations (± standard deviation) measured at MSC continental background site reached 11.5 ± 9.3 µg m^{-3} and 7.1 ± 3.9 µg m^{-3}, respectively, whereas at MSY regional background site these concentrations were 15.5 ± 7.9 µg m^{-3} and 8.2 ± 4.1 µg m^{-3} (Table S1). Thus, the continental to regional background increase is estimated in 4.0 µg m^{-3} for PM_{10} and 1.1 µg m^{-3} for PM_1 in the WMB. This increase is caused by differences of: a) altitude, b) distance to anthropogenic sources, and c) impact of atmospheric episodes. The contribution of different aerosol chemical components to this increment will be discussed in section 3.2.

A significant seasonal variation of PM_{10} and PM_1 mass concentrations was observed at both sites, with maximum values in summer and minimum in winter (Fig.2). Comparable seasonal patterns for PM_X concentrations were described for MSC (Ripoll et al., 2014) and for other regional and continental background sites in southern Europe (e.g. Cozic et al., 2008; Querol et al., 1998; Rodríguez et al., 2003; Tositti et al., 2013). In those studies the seasonal pattern has been attributed to changes in the air mass origin from summer to winter, and to the different PBL height between seasons. Moreover, at both MSC and MSY sites a secondary maximum of PM_{10} and PM_1 concentrations was observed in early spring (Fig. 2).

PM_{10} concentrations showed a stronger seasonal pattern than PM_1 concentrations at both sites (Fig. 2). This is ascribed to the higher impact of resuspended and long-range transported dust on the PM_{10} fraction, both

enhanced in summer (see section 3.3), and to the prevalence of the anthropogenic constituents in PM_1, whose emissions occur all along the year.

Comparison of these results with those from other continental background sites in Central Europe, such as Puy de Dôme at 1465 m a.s.l. in France (Bourcier et al., 2012) and Jungfraujoch at 3454 m a.s.l. in Switzerland (Cozic et al., 2008), shows that PM_{10} and PM_1 concentrations were higher at the continental background site in the WMB (Fig. S3 and Table S1). Such higher PM_{10} and PM_1 concentrations at MSC are related to the increasing role of Saharan dust particles over this area, as discussed in section 3.3 and in agreement with Ripoll et al. (2014); and to the more polluted atmosphere in summer as a result of the air mass recirculation over the WMB (Millan et al., 1997). By contrast, PM_{10} concentrations at the regional background site in the WMB were lower than those at the rural sites in Switzerland (Gianini et al., 2012) (Fig. S3 and Table S1), probably because of the specific alpine location of these sites which hinders pollution dispersion.

3.2 Continental vs. regional background aerosol chemical composition in the Western Mediterranean

3.2.1 Average aerosol chemical composition

PM_1 was mainly composed of OM at both sites (39% at MSC and 34% at MSY), followed by sulfate (17 and 21%), ammonium (7 and 6%), MM (5 and 4%), nitrate (3%), SS (1 and 2%), and EC (1 and 2%) (Fig. 3 and Table S1). The undetermined mass accounted for 27 and 28%. The $PM_{1\text{-}10}$ fraction mainly differed in the contribution of MM (55% at MSC and 39% at MSY), whereas the other components contributed similarly: OM (14 and 15%), nitrate (9 and 11%), sulfate (5 and 7%), SS (3 and 5%), ammonium (1 and 2%) and EC (0.4 and 1%). The undetermined mass was 20% at MSY and 13% at MSC. The closer compositional similarities for PM_1 fraction points to the suitability of using PM_1 as indicator of regional anthropogenic pollution in Europe, and reflects the wider spatial representativeness of the fine PM.

Overall, average absolute concentrations of chemical components were more similar between MSC and MSY for PM_1 than for the PM_{10} (Fig. 3 and

303 Table S1). The PM_1 continental to regional background increase of 1.1 µg m^{-3}
304 was attributed to the higher concentrations of PM_1 sulfate, EC, OM, and some
305 anthropogenic trace elements (V, Ni, Cu, Zn, and Pb) at the regional
306 background site. The increase of 4.0 µg m^{-3} of PM_{10} at MSY with respect to
307 MSC is attributed to higher concentrations of OM, sulfate, nitrate and SS. These
308 differences confirm that MSC is located at a sufficient altitude and distance from
309 large urban/industrial agglomerations to avoid direct anthropogenic influence
310 and to be considered a continental background site of the WMB. This also
311 confirms that MSY is more affected by the marine aerosols as it is located
312 closer to the coast. Nevertheless, MM and MM-related elements (Ti, Mn, Li and
313 Sr) PM_{10} concentrations were higher at the continental background site than at
314 the regional background site, probably due to the prevalence of long-range dust
315 transport at higher altitude layers (Sicard et al., 2011), and to the higher dust
316 resuspension at MSC.
317 In order to provide a global picture of the origin and variability of trace
318 elements in the study region, a Principal Component Analysis (PCA) was
319 performed. This exploration permitted the identification of three main common
320 groups of trace elements in PM_{10} at the continental and regional background
321 sites. Ordered by their contribution to the total mass of trace elements in PM_{10}
322 these groups were: mineral, industrial + road traffic and fuel oil combustion
323 related elements (Table S2 and Table S3).
324 In the **mineral** group typical crustal elements (Ti, Mn, Li, and Sr) were
325 included, but also V, Cr, Co, Ni, and As were partially associated with this factor
326 since these elements, usually attributed to anthropogenic sources, are also
327 found in clay mineral assemblages. The group for which high loading factors
328 were obtained for Cu, Zn, As, Cd, Pb, Sb and Sn was associated with
329 **industrial + road traffic** sources, based on previous studies which identified a)
330 Pb, Zn, Mn, and Cd as tracers of the influence of industrial activities located in
331 the surroundings of Barcelona, such as smelters and cement kilns, b) Cu, Sn
332 and Sb as tracers of non-exhaust vehicle emissions (Amato et al., 2009). These
333 sources could not be split by the PCA probably because these emissions are
334 mixed during their transportation from industrial and urban areas to MSY and
335 MSC. The **fuel oil combustion** group was better identified at MSY than at
336 MSC, and it was traced by V and Ni. These elements are typical markers of fuel

337 oil combustion, strongly influenced by shipping emissions in the study region
338 (Minguillón et al., 2014; Pey et al., 2013a).

339 Fig. S3 and S4 and Table S1 shows average concentrations of chemical
340 components in PM_{10} at the continental background site of Puy de Dôme
341 (Bourcier et al., 2012) and at the rural stations of Payerne and Magadino
342 (Gianini et al., 2012). Nitrate and ammonium PM_{10} concentrations at MSC were
343 slightly higher than those observed at Puy de Dôme, whereas the
344 concentrations registered at MSY were lower than those measured at Payerne
345 and Magadino. The similar sulfate concentrations across Europe in both
346 continental and regional background areas corroborate that this component can
347 remain in the atmosphere for long time, homogenizing sulfate concentrations in
348 Europe. Average PM_{10} concentrations of EC and OM in the WMB were lower
349 than those measured at Payerne and Magadino, probably due to the higher
350 influence of biomass burning in Central Europe. This is confirmed by the higher
351 concentrations of the well-known biomass burning tracer potassium (Pio et al.,
352 2008) registered at the Swiss stations, most of it water soluble (Gianini et al.,
353 2012). Mineral major (Al+Ca+Mg) and trace (Ti, Sr, La or Ce) elements at MSC
354 and MSY were recorded in concentrations twice as high as those at Payerne
355 and Magadino indicating the higher influence of Saharan dust transport and
356 regional dust resuspension in the Mediterranean area. As expected, a higher
357 influence of SS particles was observed at MSC and MSY than at Payerne and
358 Magadino owing to their closer location to the Mediterranean Sea. Conversely,
359 the highest concentrations of typical anthropogenic trace elements, such as Ni,
360 Cu, Zn, As, Cd, Sb, and Pb, were recorded at the Swiss stations, with the
361 exception of V which was higher at the Spanish sites. This can be partially
362 attributed to a greater influence of emissions from fuel-oil combustion, mostly
363 from shipping emissions in the Mediterranean region (Pey et al., 2009).

364 3.2.2 Partitioning of major and trace components in PM_1 and PM_{1-10}

365 In the WMB region **nitrate** showed a prevalent coarse grain size
366 distribution (Figs. 3 and S5). PM_{1-10} nitrate compounds were partially associated
367 with mineral dust and sea salt particles, since nitric acid and/or some other
368 nitrogen compounds can react with these particles (Wall et al., 1988; Zhuang et
369 al., 1999a). The resulting coarse sodium or calcium nitrates particles are much

more stable than ammonium nitrate at high temperature and low humidity (Zhuang et al., 1999b).

As expected, **sulfate** was mainly fine at both sites (Figs. 3 and S5), hence attributed to the presence of ammonium sulfate as deduced by the good ionic balance fitting between sulfate and ammonium (R^2=0.899). Nevertheless, $PM_{1\text{-}10}$ sulfate was also detected at MSC and MSY, and it was partially attributed to mineral dust and sea salt particles, and partially attributed to the reaction product between sulfuric acid and/or sulfur dioxide (SO_2) and these natural particles (Wall et al., 1988; Zhuang et al., 1999a).

Ammonium showed a prevalent fine grain size distribution at the continental and regional background sites (Figs. 3 and S5). Fine ammonium was attributed to the presence of both ammonium nitrate and ammonium sulfate. $PM_{1\text{-}10}$ ammonium is most likely in $PM_{1\text{-}2.5}$ fraction, according to Querol et al. (2009).

OM was mainly fine at both sites (Figs. 3 and S5). A high number of studies have demonstrated the dominant secondary origin of the fine OM (Jimenez et al., 2009). In the study area, previous works found that secondary organic aerosols (SOA) accounted for 91% and 55% of the OM at MSY and at the city of Barcelona, respectively (Minguillón et al., 2011; Mohr et al., 2012). Therefore, fine OM at MSC is expected to be dominated by SOA, even more than at MSY given its remote settlement. Furthermore, the presence of OM in $PM_{1\text{-}10}$, especially in spring and summer, suggests the impact of primary bioaerosols (Pöschl et al., 2010).

Despite **EC** was mainly fine at both sites (Figs. 3 and S5), $PM_{1\text{-}10}$ EC was also detected, suggesting a partial association between EC and MM by means of adsorption of anthropogenic pollutants onto dust.

As expected, most of the **MM** species and the mineral trace elements were encountered in the $PM_{1\text{-}10}$ fraction, while the concentrations in PM_1 were clearly lower at both sites (Figs. 3 and S6 and Table S1). Contrary to the rest of MM species, K was also abundant in PM_1 fraction and its concentrations were slightly higher at MSY than those at MSC (Figs. S6 and S7c). This indicates an additional source origin other than mineral (generally as K-feldspar and illite, a K-bearing clay mineral), such as biomass burning, especially over the regional background. The winter DAURE campaign performed in March 2009 revealed

that biomass burning emissions accounted for 33% of EC and 22% of OM at MSY (Minguillón et al., 2011). Nevertheless, these contributions are much lower than those obtained at other European regions (Pio et al., 2011).

SS components were found mainly in the PM_{1-10} fraction at both sites (Figs. 3 and S5) as we expected. In the continental background, the lower variation of SS concentrations as a function of atmospheric episodes reflects the minor impact of marine aerosols in this continental background area.

Most of the **trace elements** showed a prevalent fine grain size distribution at MSC and MSY (Fig. S8), especially the ones include in the industrial + road traffic group and in the fuel oil combustion group. V, Cr, Co, Ni, and As were also found in the PM_{1-10} fraction because these elements are also present in clay mineral assemblages.

3.3 Atmospheric episodes affecting continental and regional background aerosol chemical composition in the Western Mediterranean

The WMB is affected by peculiar atmospheric episodes which influence aerosol chemical composition. At MSC site higher frequency of Atlantic advections was detected, whereas MSY site was more influenced by regional episodes (Fig. 1). However, the seasonal distribution of the main atmospheric episodes throughout the year is very similar at both sites. The North African (NAF) episodes were more frequent from March to October (17% and 18% of the days, at MSC and MSY, respectively), and very often they alternated with the summer regional (SREG) scenarios (12% and 27% of the days) or both episodes occurred simultaneously, when the NAF air masses travel at high altitudes and the stagnation of air masses prevail at surface levels (Escudero et al., 2005). The winter regional (WREG) scenarios were detected from October to March (11% and 27% of the days), as well as the European (EU) episodes (11% and 13% of the days). Air masses from the Atlantic (AN, ANW and ASW) affected the WMB all along the year (62% and 41% of the days). Conversely, the Mediterranean (MED) episodes were detected sporadically (4% of the days at both sites) and therefore conclusions on their characteristics will not be drawn in the present study. Moreover, the WMB is affected by sporadic large wildfire events, especially during summer (Cristofanelli et al., 2009).

3.3.1 North African episodes (NAF)

The non-NAF to NAF increase in PM_1 concentrations is estimated in 2.9 µg m^{-3} and 4.6 µg m^{-3} at MSC and MSY, respectively, whereas this increase in PM_{1-10} concentrations is estimated in 14.3 µg m^{-3} and 7 µg m^{-3} (Figs. 4 and 5). The PM_1 non-NAF to NAF increase was attributed to the increment of PM_1 MM, sulfate, nitrate, ammonium, OM, and EC (Figs. S5 and S6). In relative contribution the highest difference in PM_1 concentrations was recorded for MM at MSC (Fig. 4) thus evidencing that NAF episodes also affect the fine fraction.

On the other hand, the higher concentrations of PM_{1-10} MM under NAF episodes accounted for the non-NAF to NAF increase of PM_{1-10} concentrations. Additionally, average concentrations of trace elements from the mineral group were higher at the continental background site than at the regional background site under NAF episodes (Fig. S6). Concentrations of nitrate and sulfate were high during NAF episodes at both sites when compared with the average (Figs. S5 and S7b). At MSY concentrations of coarse ammonium and EC also increased.

The higher impact of NAF scenarios on the continental than on the regional background aerosols in the WMB confirms that African dust travels preferentially at high altitudes. The concurrent increase of secondary pollutants (nitrate and sulfate) at MSC demonstrates that dust arrives together with industrial pollutants, as evidenced at Canary islands by Rodríguez et al. (2011). The relatively high concentrations of secondary pollutants and EC during NAF at MSY in PM_1 and PM_{1-10} can be related to the interaction of dust with anthropogenic pollutants. During NAF episodes a compression of the PBL is observed at regional scale (Alastuey et al., 2005; Pandolfi et al., 2013) (Fig. S9), and a dominance of southern winds during the whole day breaks the regular sea breeze circulation (Jorba et al., 2013). These processes enhance the concentration of regional pollutants in the lowest part of the troposphere and inhibit the sea breeze “clean up” effect.

The net contribution of African dust to the PM_{10} concentrations was estimated in 16% at MSC and 11% at MSY. This is in agreement with results presented by Pey et al. (2013b).

An example of the impact of NAF episodes on the continental and regional background aerosols was recorded on 26 March 2011 (Fig. 5b).

Backward trajectory for this day clearly showed a North African air mass origin (Fig. S10) and NAAPS model indicated high dust surface concentrations over the Iberian Peninsula (Fig. S11). During this episode, dust transport affected more strongly MSC than MSY, with PM_{10} MM concentration reaching 16 μg m^{-3} at MSC (more than 5 times higher than the annual average), and 9 μg m^{-3} at MSY (about 3 times higher than the annual average). At MSC, concentrations of MM increased simultaneously with those of sulfate (2 times higher than the annual average), nitrate (3 times) and other anthropogenic elements, such as Sb and EC, reflecting that dust is transported together with these pollutants. The increments of absolute concentrations of nitrate, sulfate, Sb and EC were higher at MSY than MSC probably due to the aforementioned effect of both the PBL compression and the breeze.

3.3.2 Summer regional episodes (SREG)

The importance of the SREG scenarios in the WMB has been studied in a number of works (e.g. Escudero et al., 2005; Gangoiti et al., 2001; Millan et al., 1997; Rodriguez et al., 2002). These episodes take place under weak barometric gradient and a lack of advections in summer, which causes the recirculation of air masses over the WMB. Generally, these situations last for several days, favoring the accumulation of pollutants at regional scale, increasing the magnitude of convection and aging processes, and enhancing the dust resuspension and the formation of secondary organic and inorganic aerosols. For these reasons, under SREG episodes high concentrations of PM_1 and PM_{1-10} were measured at the regional background site (Fig. 4). The PM_1 increase was attributed to higher concentrations of PM_1 sulfate, OM, EC and trace elements of industrial + road traffic group, and the PM_{1-10} increase was ascribed to higher concentrations of PM_{1-10} MM, OM, and EC (Figs. S5, S6 and S8).

In spite of the high altitude of MSC, the continental background site was also affected by this type of episodes due to a higher development of the PBL over the continental areas (Fig. S9), which favors the transport of anthropogenic pollutants towards high altitude sites such as MSC, and enhance the dust resuspension (Figs. 4, S5, S6 and S8).

High concentrations of elements such as Ca, Mg, Sr, and Mn during SREG scenarios (Fig. S6) confirm the local/regional origin of these dust particles at both sites. However, the ratio of concentrations of these specific elements with respect to Al during SREG scenarios was higher at MSC compared to MSY, probably because of the calcareous (richer in Ca, Mg, Sr and Mn) nature of Montsec range as opposed to the slate and granitic composition (richer in Al) of Montseny range.

3.3.3 Winter regional episodes (WREG)

The WREG episodes affecting the WMB have been described by Pey et al. (2010) as winter anticyclonic episodes (WAE), based on a comparison between urban and regional background sites. In the present study the WREG episodes showed low concentrations of PM_1 and PM_{1-10} on average (Fig. 4), but the chemical composition revealed the higher relative contribution of anthropogenic sources and the lower relative proportion of natural emissions, with high concentrations of PM_1 nitrate, ammonium, OM and EC, and the lowest concentrations of PM_{1-10} OM and MM, especially at MSY (Figs. S5, S6 and S7a).

The impact of these episodes on the continental and regional background aerosols can be explained by the persistence of anticyclonic conditions in the WMB. During these situations the stagnation of air masses occurs, which increases the pollution around the emission sources (mainly urban and industrial areas); therefore regional and continental background areas are presumably free of this anthropogenic pollution. However, the meteorological conditions (sunny days and thermal inversion) together with the topography of the WMB (very mountainous) may develop mountain breezes. In this case, the anthropogenic pollution accumulated over the adjacent valleys, reaches regional background sites and rarely continental background areas as intense pollution episodes.

Fig. 5d shows an example of a WREG episode affecting the WMB during the period 14-19 January 2012. Backward trajectory of air masses for these days corroborate a WREG situation (Fig. S10). During this episode PM_{10} nitrate, ammonium, EC and OM concentrations at the regional background site increased from 0.2 μg m^{-3}, 0.2 μg m^{-3}, 0.2 μg m^{-3} and 3.4 μg m^{-3} on 13 January

to 1.3-5.0 μg m^{-3}, 0.6-1.9 μg m^{-3}, 0.2-0.5 μg m^{-3} and 3.7-8.4 μg m^{-3} between 14-19 January 2012, respectively. Simultaneously, the continental background site was almost unaffected by such polluted air masses since nitrate, ammonium, EC and OM concentrations in PM_{10} remained between 0.1-0.6 μg m^{-3}, 0.1-0.5 μg m^{-3}, 0.05-0.13 μg m^{-3} and 2.3-4.2 μg m^{-3}, respectively.

3.3.4 European episodes (EU)

During EU episodes air masses from Central and Eastern Europe are transported towards the WMB crossing the whole continent. This type of episode is associated with cold meteorological conditions and polluted air masses (Pey et al., 2010). For this reason, under EU episodes high concentrations of PM_1 and PM_{1-10} were measured at both sites (Fig. 4). This increase was attributed to higher concentrations of nitrate, ammonium, OM, EC and trace elements of industrial + road traffic group at both fractions PM_1 and PM_{1-10}, especially at MSC (Figs. S5 and S8).

The higher impact of EU scenarios on the continental background aerosols than on the regional background aerosols, confirms that the transport of pollutants occurs preferentially at high altitude layers (between 915-1930 m), as observed by Sicard et al. (2011).

An example of the impact of EU episodes on the continental and regional background aerosols was recorded on 15 October 2011 (Fig. 5c). During this episode the air mass remained 3 days over Central Europe before reaching the WMB, as shown by the backward trajectory (Fig. S4). Under these meteorological conditions PM_{10} nitrate, sulfate, ammonium, EC and OM daily concentration at MSC reached 5 μg m^{-3} (6 times higher than the annual average), 4 μg m^{-3} (about 3 times higher than the annual average), 2 μg m^{-3} (more than 4 times higher than the annual average), 0.3 μg m^{-3} (almost 3 times higher than the annual average) and 6.4 μg m^{-3} (about 2 times higher than the annual average), respectively. Simultaneously, the regional background site was less affected by this episode as PM_{10} nitrate, sulfate, ammonium, EC and OM concentrations at MSY were 2.3 μg m^{-3} (1 μg m^{-3} higher than the annual average), 2.0 μg m^{-3}, 0.2 μg m^{-3}, 0.2 μg m^{-3} and 3.2 μg m^{-3}, respectively.

3.3.5 Atlantic advections (AN, ANW, ASW)

The WMB is strongly affected by oceanic air masses owing to the high influence of Atlantic winds over this region, which is favored by the displacement of the Azores High westwards or southwards, allowing the movement of depression systems towards the Mediterranean (Lopez-Bustins et al., 2008). This type of episodes is associated with increased precipitation and intense winds, which favors the atmospheric wet-scavenging processes, leading to the renovation of the regional aged air masses.

These meteorological conditions explain why low PM_1 and PM_{1-10} concentrations were measured under Atlantic advections at both sites (Fig. 4) and for most of the aerosol chemical components (Figs. S5, S6 and S8).

3.3.6 Wildfire events

Although biomass burning is not a major source in the WMB, some contribution of biomass burning is observed and partially attributed to wildfires. Therefore, high concentrations of PM_1 OM and EC during NAF and SREG episodes (Fig. S5) were partially ascribed to higher frequency of wildfires, since these episodes very often occur simultaneously.

Fig. 5e illustrates the impact of a wildfire on continental and regional background aerosols in the WMB. This event took place in Eastern Europe on 27-28 March 2012, as shown by the NAAPS model with high smoke surface concentrations over SE Europe (Fig. S11). Backward trajectory for these days clearly showed a transport of air masses from SE Europe towards the WMB (Fig. S10). During this episode, daily PM_{10} OM and EC concentration at MSY reached 7.9 µg m^{-3} (almost 2 times higher than the annual average) and 0.3 µg m^{-3} (1.5 times higher than the annual average), respectively, and at MSC it was 9.1 µg m^{-3} (almost 3 times higher than the annual average) and 0.3 µg m^{-3} (3 times higher than the annual average). Moreover, K concentrations in PM_{10} at MSY reached 0.27 µg m^{-3} (2 times higher than the annual average), with a prevalent fine partitioning (PM_1/PM_{10}=0.55), instead of its main coarse occurrence (PM_1/PM_{10}=0.28) during NAF episodes, which confirms the biomass burning origin.

3.4 Seasonal variation of continental and regional background aerosol chemical composition in the Western Mediterranean

In addition to the atmospheric episodes discussed above, the aerosols in the WMB are also affected by the different evolution of the PBL height and differences in the meteorological parameters throughout the year. In the warmer months (April-September) the development of the PBL at MSC is much more relevant than that at MSY (Figs. S2 and S9) owing to the higher convection at the continental background sites (Rodriguez et al., 2002), and to the higher cooling effect from the sea breeze at the regional background sites. On the other hand, in the colder months (October-March) the lower vertical development of the PBL at the inland sites leaves MSC in the FT on most days, whereas the regional background site is located most of the day within the PBL (Fig. S2).

Nitrate concentrations decreased in summer at both sites, especially in PM_1 (Fig. 6) (2 and 3 times lower than the winter concentrations at MSC and MSY, respectively). This decrease was attributed to the high volatility of ammonium nitrate (Pey et al., 2009) at low humidity and high temperature (Zhuang et al., 1999b). During the colder months higher nitrate concentrations are associated to WREG episodes at MSY and to EU episodes at MSC, with the exception of the November-to-January period, when MSC is mostly within the FT and therefore low nitrate concentrations were registered.

Sulfate showed similar seasonal variations at both sites and relatively similar absolute concentrations, with the highest values during the warmer months (3 and 2 times higher than the winter concentrations at MSC and MSY, respectively) (Fig. 6). The squared Pearson correlation coefficient between the daily sulfate concentrations at MSC and MSY was 0.71. This similarity reflects the high stability of sulfate and its longer residence time in the atmosphere resulting in a homogeneous sulfate concentration in the WMB. The summer maximum was likely due to the higher photochemistry in the atmosphere that enhances the SO_2 oxidation (6% h^{-1} in summer vs <1% h^{-1} in winter, Querol et al., 1999), and to the accumulation of pollutants over the WMB as a result of the SREG and NAF episodes. Additionally, regional background sulfate aerosols in summer could be affected by the transport of shipping emissions from the Mediterranean to the continental areas, due to the more intense sea breeze

633 circulation at MSY. The lower concentrations during the colder months were
634 attributed to the lower rate of SO_2 oxidation (Querol et al., 1999), and at MSC to
635 the FT conditions.
636 **Ammonium** concentrations did not follow a clear seasonal pattern (Fig.
637 6) due to its association with both sulfate and nitrate.
638 **Organic matter** concentrations followed a similar seasonal variation at
639 both sites, with the highest values during the warmer months (1.8 and 1.5 times
640 higher than the winter concentrations at MSC and MSY, respectively) (Fig. 6).
641 The summer maximum was due to: 1) the higher temperature and
642 photochemistry in the atmosphere that enhances the formation of SOA; 2) the
643 accumulation of pollutants over the WMB owing to the occurrence of SREG and
644 NAF episodes; 3) the greater biogenic emissions from vegetation (Seco et al.,
645 2011); and 4) the higher frequency of wildfires. Furthermore, at MSY a
646 secondary maximum of OM concentrations occurred in October-March linked to
647 the occurrence of WREG episodes. The continental background site was less
648 affected by this type of episodes, since MSC is mostly within the FT in winter.
649 **Elemental carbon** showed high concentrations in the warmer months at
650 MSC and a less marked seasonal variation at MSY (Fig. 6). The smoother
651 seasonal variation at MSY reflects the regional anthropogenic influence on the
652 levels of this component, since anthropogenic emissions occur all along the
653 year. The higher summer EC concentrations at both sites (more elevated at
654 MSY) were attributed to the impact of the SREG and NAF episodes, and to the
655 higher occurrence of wildfires. Additionally, at MSY high concentrations of EC in
656 summer may be caused by the higher transport of shipping emissions. The
657 increase of EC during the colder months was not registered simultaneously at
658 both environments (Fig. 6) because at the regional background site it was
659 attributed to the impact of WREG episodes, whereas at the continental
660 background site it was associated with EU episodes.
661 **Mineral matter** concentrations and mineral trace elements in the WMB
662 are driven by the local and regional dust resuspension and by the contribution
663 of African dust outbreaks, both enhanced in the warmer months. Consequently,
664 the highest values were measured in summer and the lowest in winter, with
665 sporadic high concentrations in March-April (Figs. 6 and 7).

Trace elements concentrations of the industrial + road traffic group showed low variations, especially at MSY (Fig. 7), since anthropogenic emissions occur all along the year. Fuel oil combustion elements showed a marked seasonal pattern at both sites, with the highest values in summer (Fig. 7) due to the higher shipping emissions and the more frequent and intense sea breeze circulation, which enhances the transport of air masses from the Mediterranean Sea.

4 Conclusions

Aerosol chemical characterization (PM_1, PM_{1-10} and PM_{10}) and its time variation were studied during January 2010-March 2013 simultaneously at a continental (Montsec, MSC) and a regional (Montseny, MSY) background site in the Western Mediterranean Basin (WMB).

In this particular region of the WMB, the continental to regional background increase was estimated to be 4.0 μg m^{-3} for PM_{10} and 1.1 μg m^{-3} for PM_1. Relative chemical composition and absolute concentrations of PM_X showed very similar values at both environments, especially in PM_1, in spite of their altitudinal and longitudinal differences. The similarities are more pronounced in the warmer months, when recirculation processes at a regional scale are recurrent in the WMB, and a strong development of the PBL occurs over continental areas, favoring the transport of anthropogenic pollutants towards remote sites such as MSC. These processes cause a homogenization of PM_1 concentration and composition through the region, allowing us to consider PM_1 as a more suitable indicator of anthropogenic impact than PM_{10}. Moreover, the higher temperature and solar radiation in the warmer months augments atmospheric photochemistry, promoting the formation of secondary inorganic and organic aerosols and thus incrementing markedly the concentration of certain components such as sulfate and OM. Additionally, sea breeze circulation is enhanced, favoring the transport of shipping emissions from the Mediterranean to the continental areas increasing the concentrations of sulfate, EC, and fuel oil combustion-related trace elements, especially at the regional background since it is located closer to the coast. Furthermore, the occurrence of wildfires across the WMB increases in summer, which contributes to an extra increment of the OM and EC concentrations. Conversely, nitrate is

699 not abundant in summer due to the high volatility of ammonium nitrate at high
700 temperatures and low humidity. In the colder months the lower vertical
701 development of the PBL leaves MSC in the FT on most days, whereas MSY is
702 frequently located within the PBL due to its lower elevation. As a result, very low
703 concentrations of all chemical components are recorded at MSC in winter, while
704 MSY is regularly affected by nearby polluted air masses, which enhanced the
705 concentrations of PM_X components.
706 The seasonal variation of major and trace PM_X components was also
707 governed by changes in the air mass origin from summer to winter. Whereas
708 southern flows and regional recirculation episodes are more frequent in
709 summer, Atlantic advections and northeastern winds from mainland Europe are
710 more common in winter. As a result, African dust outbreaks and regional dust
711 resuspension increase MM concentrations over the WMB in the warmer
712 months. This MM increase affects both PM_1 and PM_{1-10} and it is frequently more
713 pronounced at MSC, since long-range transport of dust occurs preferentially at
714 high altitude layers and dust resuspension is enhanced by the drier surface and
715 higher convection at this site. During NAF episodes concentrations of nitrate
716 and sulfate also increase, demonstrating that dust arrives together with
717 industrial pollutants. Moreover, a compression of the PBL and a change in the
718 wind regime towards a permanent southern flow, increments the concentrations
719 of regional pollutants (sulfate, EC and industrial and traffic tracers) in the lowest
720 part of the troposphere. Regional recirculation of air masses (SREG episodes)
721 also accounts for the accumulation of airborne particulates, increasing the
722 concentrations of sulfate, OM, EC, industrial, traffic, and fuel oil combustion
723 tracers at both continental and regional background environments.
724 In the colder months, the predominance of clean Atlantic advections
725 prevents the accumulation of regional pollution, and consequently reduces the
726 concentration of all chemical components at both sites. However, the sporadic
727 transport of polluted air masses from Central and Eastern Europe towards the
728 WMB increases the concentrations of nitrate, OM, EC, and industrial and traffic-
729 related trace elements. The impact of these polluted air masses on the
730 concentrations of PM_X components is usually higher in the continental
731 background, since this transport from Europe occurs preferentially at high
732 altitude layers. Occasionally, intense peaks of nitrate, OM and EC are

733 measured at the regional background site during the winter anticyclonic
734 episodes (WREG). These stagnant situations cause the accumulation of
735 pollutants around the emission sources (such as the Barcelona metropolitan
736 area), and pollutants can be transported towards relatively nearby areas under
737 favorable conditions. The distance from MSC to large anthropogenic sources
738 and its altitude are restricting factors for the occurrence of this process.
739 Finally, the comparison of these results with those from other continental
740 and regional background sites in Central Europe shows that African dust
741 transport and regional dust resuspension are much more important in the
742 Western Mediterranean area. The net contribution of African dust to the PM_{10}
743 concentrations was estimated in 16% at MSC and 11% at MSY. This is
744 reflected in more elevated concentrations of mineral elements across the
745 Mediterranean, with the only exception of potassium, higher in Central Europe
746 due to the contribution of biomass burning emissions. The surprising similar
747 sulfate concentrations across Europe in both continental and regional
748 background environments is probably linked to the long residence time of
749 sulfate aerosols in the atmosphere. On the contrary, nitrate and ammonium
750 showed different concentrations as a function of site, and nitrate maximum
751 concentration was observed in winter in the WMB whereas in the Central
752 Europe continental environments it was measured in summer. Moreover, the
753 highest concentrations of typical anthropogenic trace elements were recorded
754 at some European rural environments, with the exception of V which was higher
755 in the Mediterranean area due to the greater influence of shipping emissions.
756 The concurrent monitoring of aerosols properties in continental and
757 regional background sites in the WMB provides a complete picture of the
758 aerosol phenomenology of this region. In view of the relatively high
759 concentrations of atmospheric aerosols from a variety of natural and
760 anthropogenic sources, and taking into account the importance of atmospheric
761 processes. The simultaneous characterization of atmospheric aerosols at
762 continental and regional background sites feeds with valuable information policy
763 makers, and air quality and climate models.
764
765 *Acknowledgements*. This study was supported by the Ministry of
766 Economy and Competitiveness and FEDER funds under the PRISMA

(CGL2012-39623-C02-1) and CARIATI (CGL2008-06294/CLI) projects, and by the Generalitat de Catalunya (AGAUR 2009 SGR8 and the DGQA). The research received funding from the European Union Seventh Framework Programme (FP7/ 2007-2013) ACTRIS under grant agreement n^{o} 262254. The authors would like to extend their gratitude to the personnel from the COU and the OAdM. We would also like to express our gratitude to the NOAA Air Resources Laboratory (ARL) for the provision of the HYSPLIT transport and dispersion model, and boundary layer height calculation, used in this publication.

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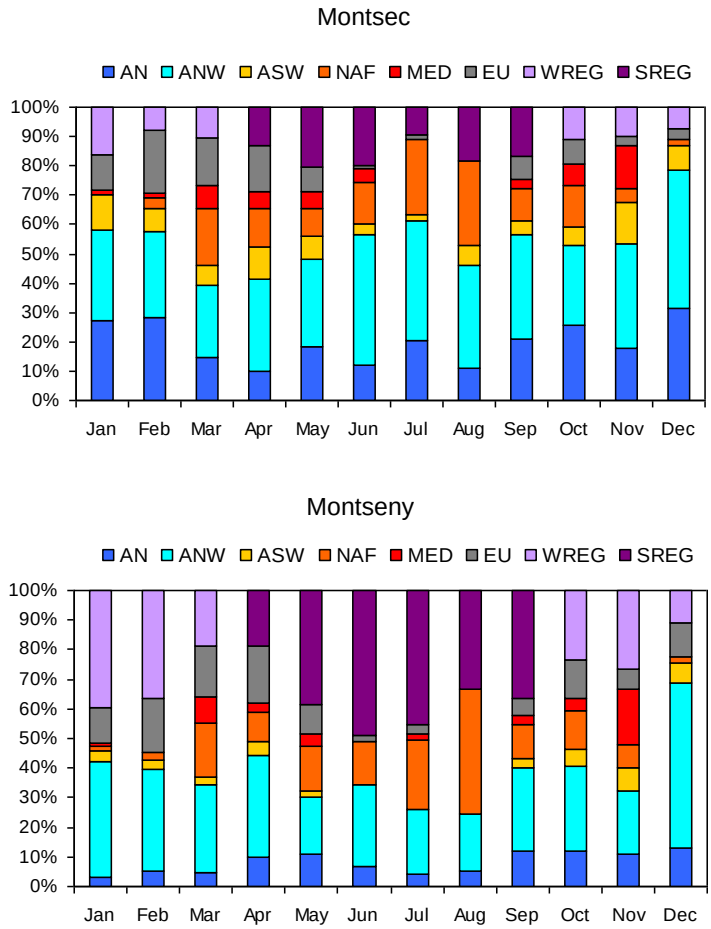

Fig. 1 Average frequency of air mass origin at Montsec and Montseny for the different months based on daily calculations between January 2010 and March 2013.

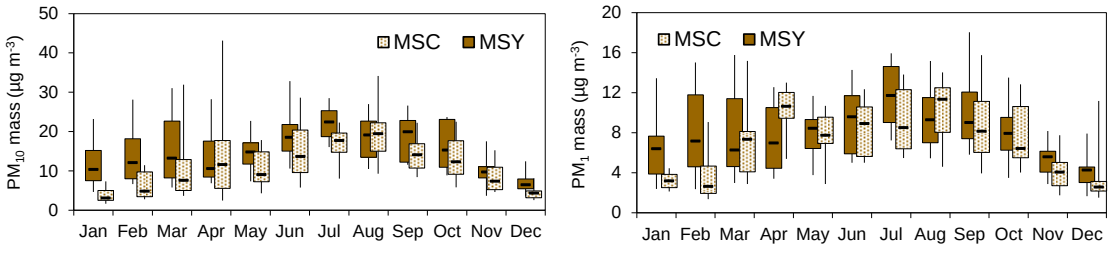

Fig. 2 Monthly median (black line within the boxes) and percentiles (5-25-75-95, boxes and whiskers) of daily PM_{10} and PM_1 mass concentrations at Montsec (MSC) and Montseny (MSY) based on daily measurements between January 2010 and March 2013.

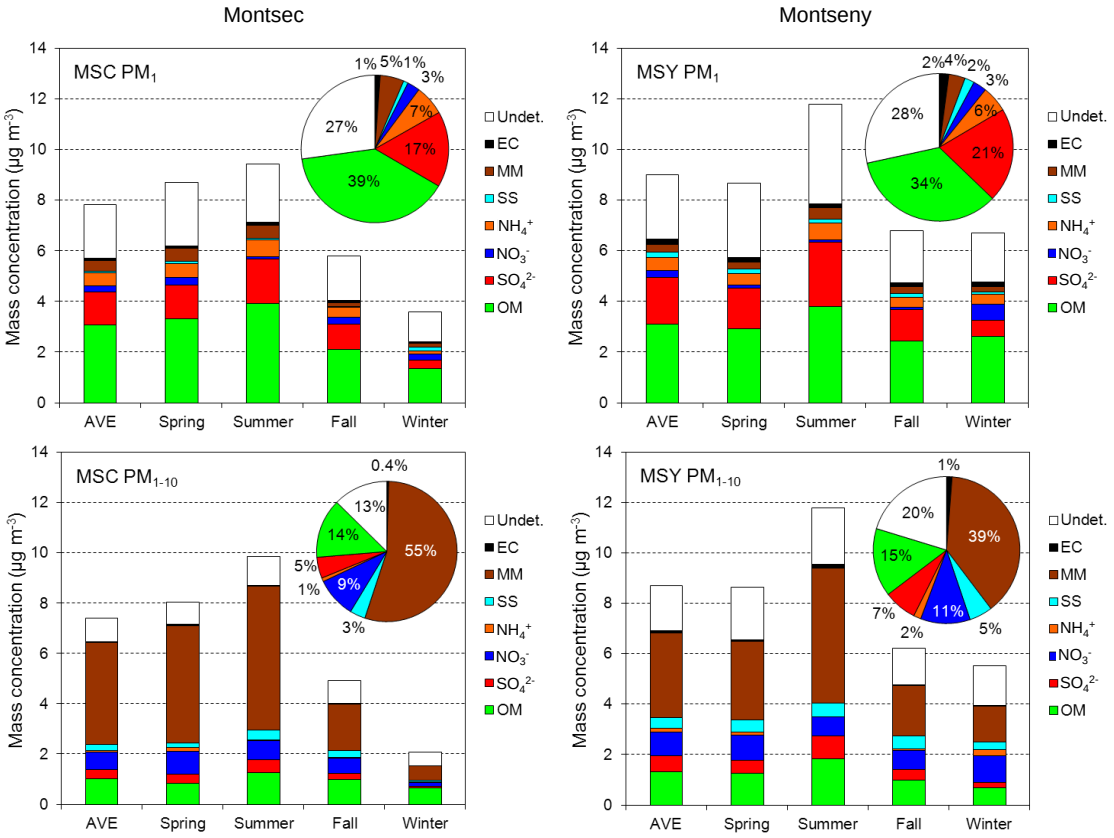

Fig. 3 Average concentrations of aerosol major components in PM_1 and PM_{1-10} fractions at Montsec and Montseny for the whole period (AVE) and for different seasons based on daily measurements between January 2010 and March 2013. Pie charts represent the average relative contribution of aerosol major components to total mass for each fraction.

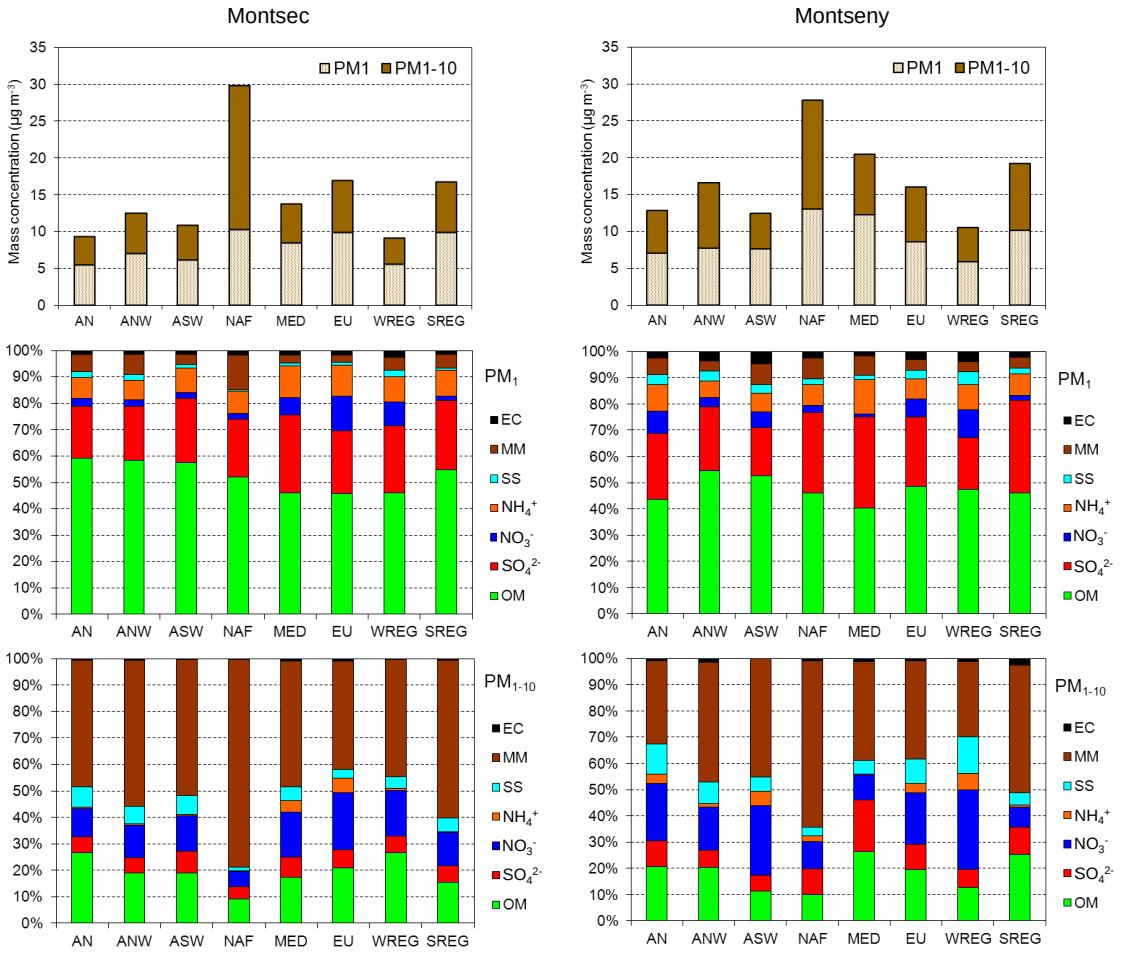

Fig. 4 Average concentrations of PM_1 and PM_{1-10} mass and relative contribution of aerosol major components in PM_1 and PM_{1-10} fractions for different meteorological episodes at Montsec and Montseny based on daily measurements between January 2010 and March 2013.

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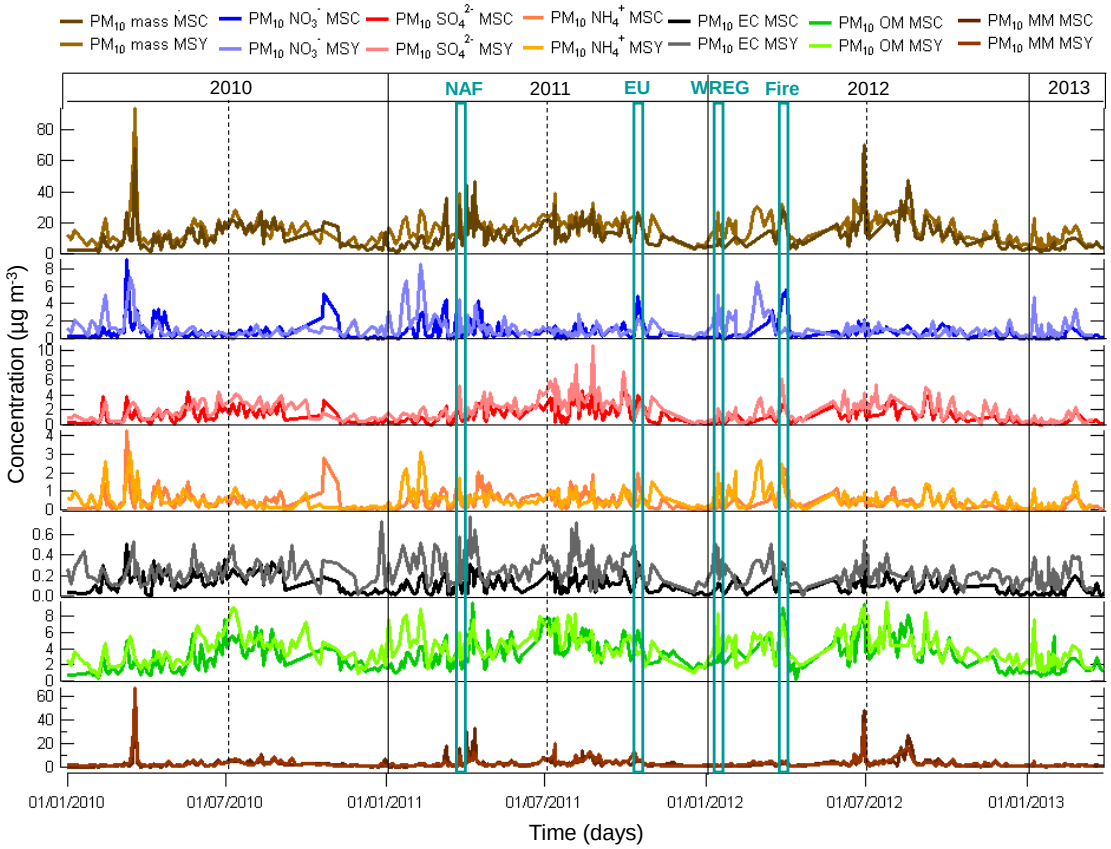
a)



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b)

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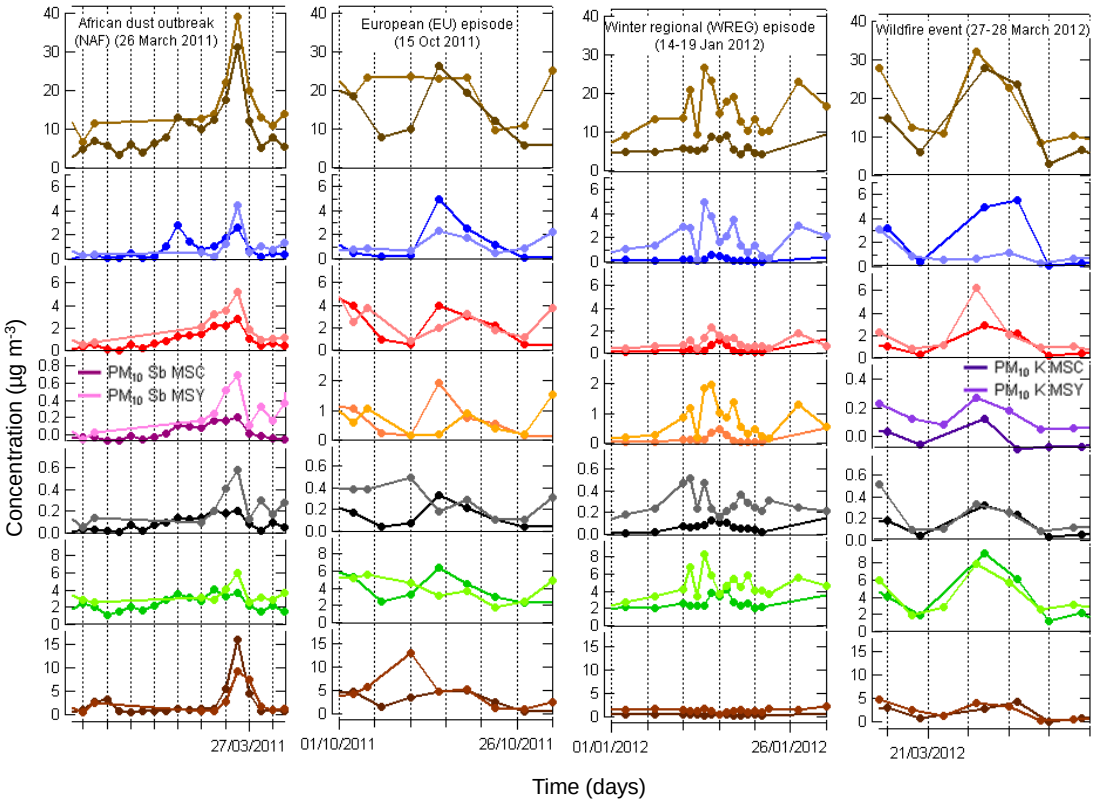

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Fig. 5 (a) Time series of daily PM_{10} mass and major PM_{10} chemical components concentrations at Montsec (MSC) and Montseny (MSY) between January 2010 and March 2013. Green bands indicate 4 examples of different episodes affecting the study area. Zoom of the 4 selected meteorological episodes: (b) African dust outbreak, (c) European episode, d(d) winter regional episode, and (e) wildfire event, with daily PM_{10} mass and PM_{10} chemical components concentrations.

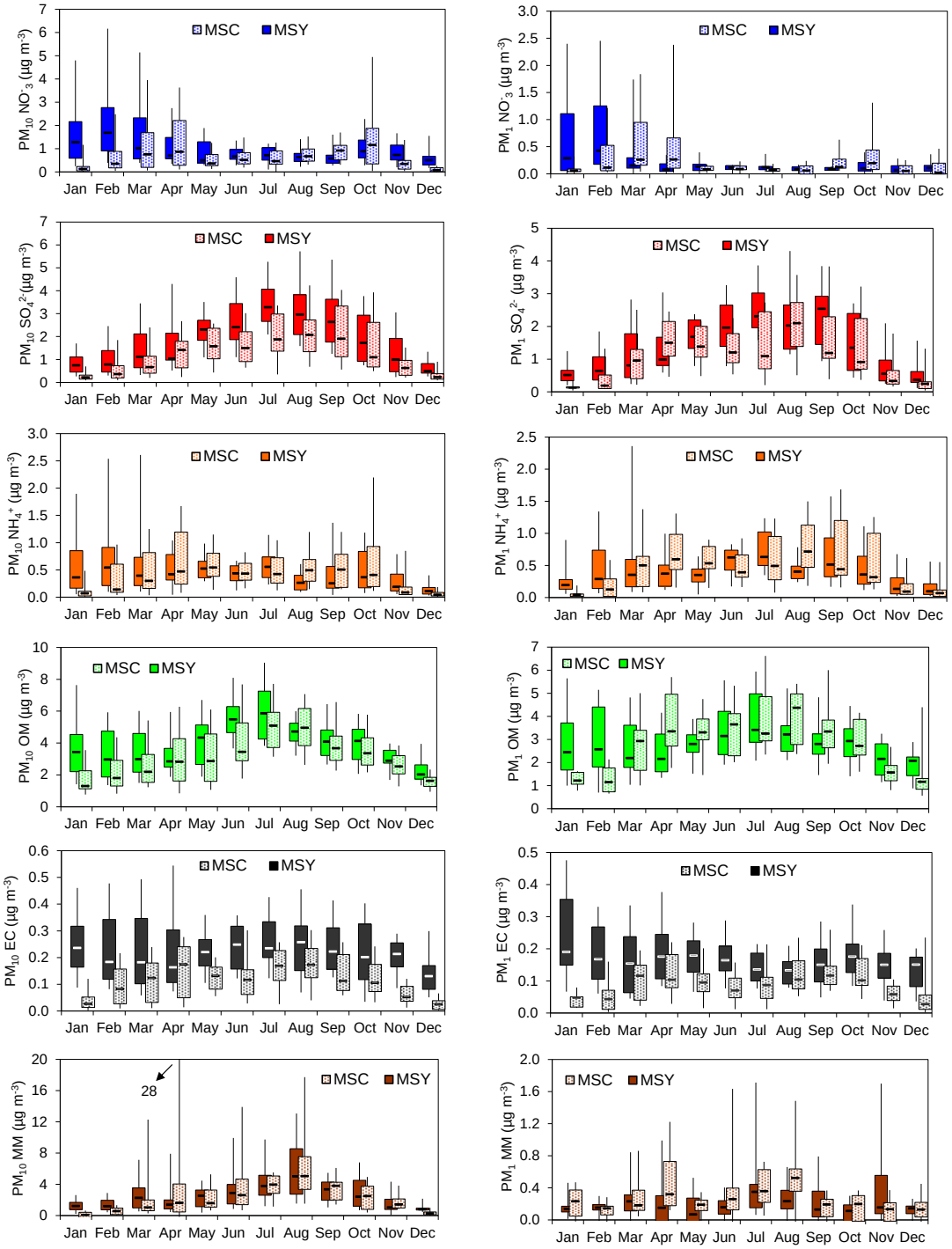

Fig. 6 Monthly median (black line within the boxes) and percentiles (5-25-75-95, boxes and whiskers) of major PM_{10} and PM_1 chemical components concentrations at Montsec (MSC) and Montseny (MSY) based on daily measurements between January 2010 and March 2013.

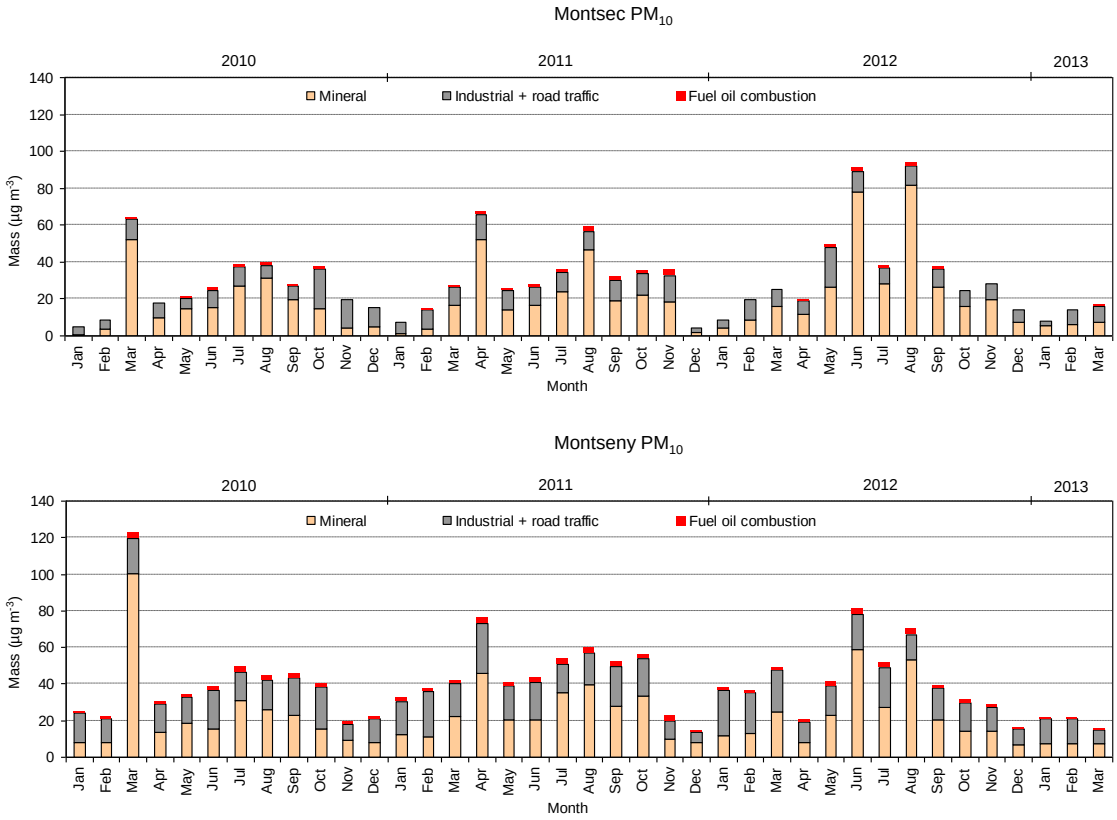

Fig. 7 Monthly average concentrations of trace element groups at Montsec and Montseny based on daily measurements of PM_{10} between January 2010 and March 2013.