

## AUTHORS' RESPONSE TO REFEREES

The authors are grateful to both referees for their generally supportive comments on this work, and for agreeing to review a particularly long and detailed manuscript. The suggestions and comments made to the manuscript have been taken into full consideration when producing the revised version of the manuscript, and they have helped to improve the quality of the paper. The response to each of the suggestions and comments is written below in a point by point manner.

### **REFEREE#1**

#### **Overall**

**This paper gives an overview of the chemical characteristics of PM<sub>10</sub> and PM<sub>1</sub> at a continental and a regional background site in Northern Spain, sites that are representative for background conditions in the Western Mediterranean Basin. The PM concentration and its chemical characteristics at the regional and continental background site are thoroughly compared, taking different meteorological regimes into account. The results are discussed in the context of data from other regional and continental background sites in France and Switzerland. The conclusions drawn are justified by the data and convincing. The paper is very well written and has a good and appropriate length, the information provided in the main text and in the supplementary material is well balanced. So I found this a very good and informative paper that should be published in Atmospheric Chemistry and Physics. It can be published more or less as it is; I have only some minor comments that should be considered for a final revised version.**

#### **Minor comments and suggestions:**

**Page 16004, line 2: Should note something like “southern Europe/the northern Mediterranean region”.**

In this case, the definition of regional background environments is given as a general description. For this reason the authors did not refer to any particular area.

“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.”

**Page 16006, line11: Should note “PM10 and PM1 sampling ...”.**

The text has been modified as follows:

“PM<sub>10</sub> and PM<sub>1</sub> sampling began in November 2009 and in March 2011, respectively.”

**Page 16007, line 27: The authors state in a single sentence that the performed chemical analyses accounted for 60-90% of total PM mass. The undetermined fraction appears rather large. The authors should add a brief discussion about the possible nature of the unidentified fraction (missing compounds, analytical reasons, etc.).**

As suggested, the possible nature of the undetermined mass has been added to the revised version of the manuscript as follows:

“Overall, the aforementioned components accounted for 60–90% of the total PM mass. Most of the undetermined mass was attributed to water not eliminated during filter conditioning in the presence of hygroscopic species, but a contribution from sampling artifacts and from the use of factors to determine CO<sub>3</sub><sup>2-</sup>, SiO<sub>2</sub>, and OM cannot be discarded.”

**Section 2.3: Please refer to Figure S5, which gives the information about the frequencies of the meteorological classes.**

The Figure S5 of the old version of the manuscript is now the Figure 1 and it has been included in section 2.4 as follows:

“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).”

**Page 16008, line 23: “... which uses the information for stability time series”. This information is probably not sufficient for readers. Please give more details what this means, or provide a reference. I would appreciate, if the authors**

**could discuss in more details about the quality and limitations of PBL height estimates based on HYSPLIT.**

The text has been modified as follows:

“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. S4).”

The authors are aware of the limitations of PBL height estimates based on READY model. This model uses a 50 km resolution grid. Since this horizontal resolution is not very good for mountain regions such as MSC (1000 m peak in just 20 kms) and MSY (Fig. S1 bottom), the estimate average terrain height from the model is around 580 m and 400 m for MSC and MSY, respectively, whereas the real altitude of these sites is 1570 m and 750 m. Furthermore, the model gives only the PBL height every three hours and we assumed that the PBL height does not change during the next three hours after the datapoint. These limitations have to be considered when analyzing the data as a function of the PBL height. To include these limitations in the revised version of the manuscript, the following text has been added:

“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.”

**16009, line 19: I think that “more important” is not the correct expression here, please change.**

The sentence has been moved to section 3.4 and rephrased as follows:

“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 ...”

**Page 16017, line 24: Replace “latest” by “latter”.**

The paragraph has been moved to section 3.2.2 and the sentence has been eliminated. The text in the new version of the manuscript is written as follows:

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

**Page 16020, line 4: Should be capital K in K-feldspar and K-bearing.**

This has also been moved to section 3.2.2 and the text has been changed as follows:

“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.”

**REFEREE#3**

**Overall**

The paper analyses a large database of PM1 and PM10 chemistry in two sites in Spain, with respect to seasonality, meteorological regimes, air mass origin, and local site characteristics such as boundary layer development. A large amount of information and analyses is provided. Good arguments are made to explain observations of higher and lower concentrations of PM and of individual chemical constituents. Particularly interesting results are the findings of transport of mineral dust and pollution to the mountain site in higher atmospheric layers, and the differing seasonal cycles of chemical constituents at the two sites. The paper is long and somewhat difficult to read in its current organization. The information of the effects of air mass origin and other processes is dispersed over many sections. Explanations for observations (mostly differences in averages of absolute concentrations) are sometimes given without consideration of possible additional effects or alternative causes. I recommend publication after reorganization and after consideration of other points as follows.

The authors are grateful to referee#3 for the suggestions and comments made to the manuscript. We have accepted most of the suggestions especially the re-organization of the section 3 (results and discussion). We hope that now the paper is easier to read.

**General comments:**

**1. Organization**

Currently, the text requires frequent (and exhausting) jumping back and forth between figures, and between the main text and the supplement. There are long stretches of text, especially at the beginning (in Sections 2.3, 3.1 and 3.2.0) and at the end of the paper (in Section 3.2.8) that depend heavily on figures and tables provided in the supplement, making the supplement crucial for the understanding of the main text, and amounting, in effect, to a much longer paper.

The authors acknowledge the inconveniences of using too many figures but our intention is to illustrate as well as possible all the information we wanted to show and unfortunately this requires quite a high amount of figures. Details on the re-organization of the text and the figures are given in the below replies.

**The following figures are needed in the main text, rather than in the supplement:**

**Figure S1: geography/topography of the two sites**

**Figure S4: relative concentrations**

**Figure S5: air mass origins and their seasonality**

The authors agree that some figures are needed in the main text. Figure S5 is Figure 1 in the new version of the manuscript and Figure S4 has been combined with Figure 1 and it is now Figure 3. However, the authors think that Figure S1 should remain in the supplement as it is already partially published in the main text of Ripoll et al. (2014) and partially in Pérez et al. (2008) as it is referred in the main text (page 16006 line 3 and line 8). Moreover, in the first version of the manuscript we already decided to include Figure S1 in the supplement in order to reduce the number of figures in the main text.

**Figure 2 and Figure 5 should be omitted from the main text and moved to the supplement, as they are not discussed in great detail.**

As suggested, Figure 5 has been moved to the supplement and it is now Figure S3. Nevertheless, the authors think that Figure 2 should remain in the main text as it is referred 13 times and show clearly the seasonal trend, it is now Figure 6. Furthermore, Figure 3 and Figure 6 have been moved to the supplement and they are now Figure S5 and Figure S6.

**The following figures should be omitted altogether, in the interest of reducing the amount of material to digest:**

**Figure S2: As a similar data schedule for MSY is missing, this figure is incomplete. The MSC sampling schedule is already partly described in words in section 2.1. The total number of sampling days at MSC (as done for MSY), exact dates of the intensive campaigns can be added there, as well as detailing longer measurement gaps.**

**Figure S6: this figure is currently only referred to in conjunction with other figures in the main text, and only in the context of discussing absolute concentration values, thus no new information is added.**

**Figure 8: is discussed in only very briefly at the very end of the paper, partly repeating conclusions reached earlier in the paper.**

The authors agree that Figure S2 can be eliminated from the supplement. However, we think that the supplement is used to give further information or to add extra figures which in many cases show the same information but in different way and help to understand the concepts of the manuscript. For these reasons, the supplement should not be limited and the authors prefer keeping the Figure S6 (which is now Figure S7). Moreover, Figure 8 has been moved to the supplement and it is now Figure S4.

The revised manuscript has 7 figures and the supplementary information contains 11 figures.

**It would greatly enhance readability if Section 3.2 was re-organized by process, i.e. split into a section on general chemical differences between the two sites (Figure S4), a section on seasonal differences and BL development (Figure 1 and Figure 2, a section on differences by air mass (Figures 3 and 6), and a section dealing with the air mass case studies (Figure 4) - that way, the figures would be discussed in order, requiring less jumping around, and the impacts of the various processes would be easier to understand. Repeated discussion of similar trends in different species governed by the same process (e.g. common trends of species associated with anthropogenic pollution, p. 16017 line 17-19; increased pollution due to BL compression in NAF episodes, p. 16014 line 19, again in p. 16018, line 4, and again in p. 16022 line 14; discussion of shipping emissions p.16015 line 9, again in p. 16018 line 10, and again in p. 16023 line 3) would be avoided and the paper thus shortened.**

The authors are aware of the inconveniences of discussing trend variations of several components affected by different factors at the same time and for this reason we tried our best to not repeat too much, but even so it is very difficult to synthesize all the information and not repeat too much. The very early version of the manuscript was written by sections of processes, as it is suggested by the reviewer here, but authors decided to change the initial organization in sections by scenarios to sections by components (ACPD version of the manuscript) to shorten the total length of the manuscript and to avoid repetitions. Nevertheless, we have accepted the re-organization proposed and we have striven hard to write the revised version of the manuscript as synthetic as possible and with the minimum repetitions.

In the new version of the manuscript the results and discussion section has been divided in:

- 3.1 *Continental vs. regional background PM concentrations in the Western Mediterranean*
- 3.2 *Continental vs. regional background aerosol chemical composition in the Western Mediterranean*
  - 3.2.1 Average aerosol chemical composition
  - 3.2.2 Partitioning of major and trace components in PM<sub>1</sub> and PM<sub>1-10</sub>
- 3.3 *Atmospheric episodes affecting continental and regional background aerosol chemical composition in the Western Mediterranean*
  - 3.3.1 North African episodes (NAF)
  - 3.3.2 Summer regional episodes (SREG)
  - 3.3.3 Winter regional episodes (WREG)
  - 3.3.4 European episodes (EU)
  - 3.3.5 Atlantic advections (AN, ANW, ASW)
  - 3.3.6 Wildfire events
- 3.4 *Seasonal variation of continental and regional background aerosol chemical composition in the Western Mediterranean*

**The section on trace metals currently does not add a lot of new insight. While the method is interesting in principle, its description is too short, results are buried at the end of an already long paper, and much interesting information (components by air mass, factor loadings and explained variance) is hidden in the supplement. The (short) interpretation currently largely repeats anthropogenic vs. dust-related trends discussed at earlier points in the paper. Should the authors decide to retain the trace metal analysis, the PCA method needs to be explained in Section 2. If Section 3.2 is re-organized as suggested above, focused results from the trace metals analysis could then be added where relevant, instead of trying to explain all the observed trends (some of which are the same as already explained in the discussion of major chemical constituents) in a whole separate section.**

The authors acknowledged the inconveniences of showing too many results in a single paper but we think that trace elements results are very interesting as no many papers analyze trace elements in PM<sub>10</sub> and PM<sub>1</sub>. For this reason we prefer to keep the trace elements results. As suggested, the trace elements results have been added

along the text where they are relevant instead of explaining all of them in an extra section.

The PCA method explanation has been included in section 2 as follows:

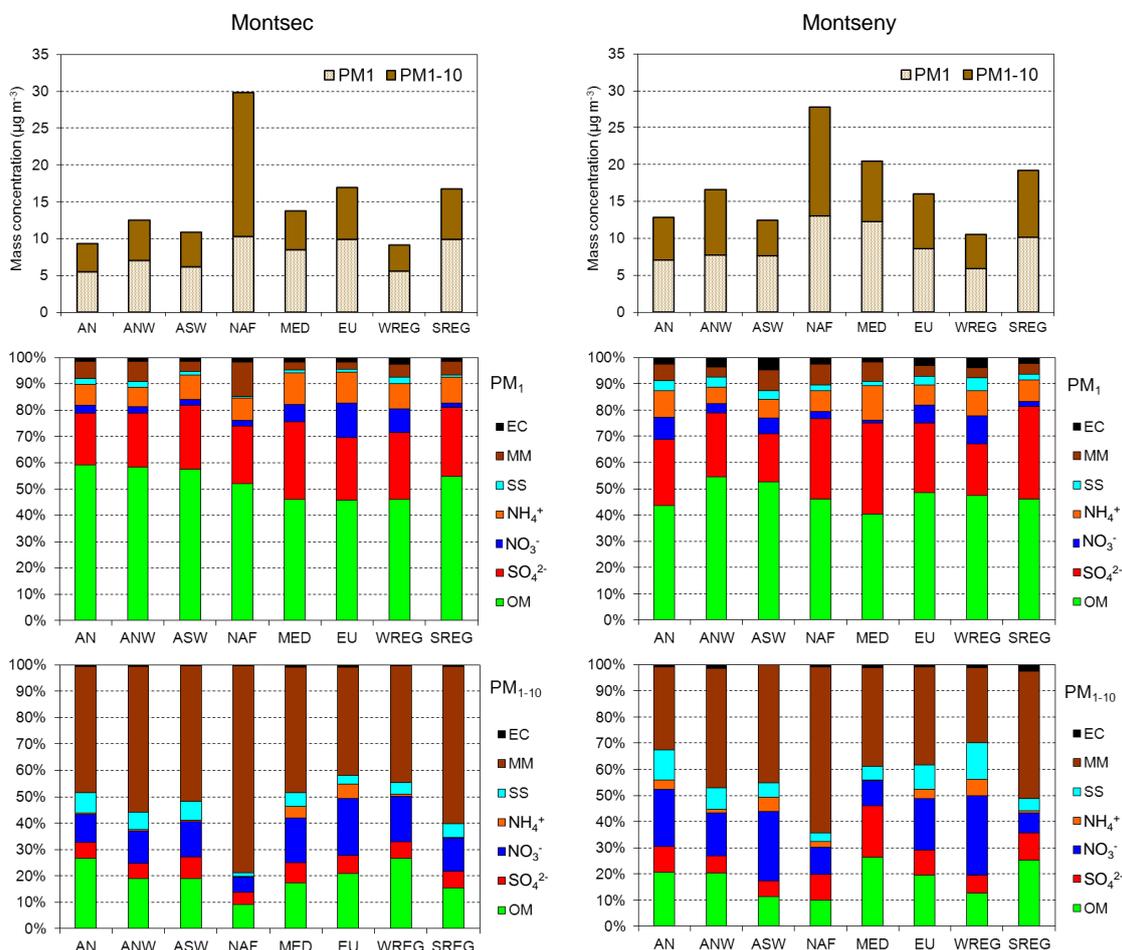
### *“2.3 Principal component analysis*

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<sub>10</sub> constituents Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, SO<sub>4</sub><sup>2-</sup>, Al<sub>2</sub>O<sub>3</sub>, 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<sub>10</sub> 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<sub>10</sub> at the continental and regional background sites.”

## **2. Methodology:**

**One major issue with the way the data are currently presented is the discussion of constituents (nitrate, organic matter, etc.) in terms of absolute concentrations, rather than in terms of relative contributions to PM10 or PM1. It is hard for the reader to distill information on changing chemical characteristics with air mass or BL development, having to keep general mass trends in mind. BL development in particular leads to large dilution and concentration effects, so it would be more insightful to discuss chemical trends in terms of relative contributions (e.g. p. 16014 lines 19-22). The paper already includes a discussion of PM10 and PM1 (Section 3.1) – this section could be expanded, thoroughly discussing the effects of BL development and air mass origin (both as a function of season) on PM1 and PM10 concentrations. The sections discussing the individual chemical constituents (3.2.1 – 3.2.7) could then focus on deviations from the general mass trends, and on the changes in relative contributions of these constituents to PM1 and PM10 with changing BL development, air masses etc. This would likely shorten the paper, as general mass trends would not have to be repeatedly explained when discussing individual constituents (e.g. p.16012 line 19 and following, p. 16011 line 23, p. 16014, line 2, p. 16016 line 5, p. 16017 line 15).**

The authors agree that relative contributions of major chemical components to the total  $PM_1$  and  $PM_{1-10}$  mass is a better way to show changes in chemical characteristics as a function of atmospheric episodes. For this reason, we have replaced Figure 3 and Figure 6 (now Figure S5 and Figure S6) by Figure 4:



**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.

Another issue is the fact that averages are compared, but much of the discussion is rather qualitative (“lower” and “higher” concentrations). Standard deviations are rarely given or commented on; the statistical significance of the many differences between averages (even when one average is only “slightly higher” than another) is not stated.

As suggested, standard deviations have been included in the text as follows:

“ $PM_{10}$  and  $PM_1$  average concentrations ( $\pm$  standard deviation) measured at MSC continental background site reached  $11.5 \pm 9.3 \mu g m^{-3}$  and  $7.1 \pm 3.9 \mu g m^{-3}$ ,

respectively, whereas at MSY regional background site these concentrations were  $15.5 \pm 7.9 \mu\text{g m}^{-3}$  and  $8.2 \pm 4.1 \mu\text{g m}^{-3}$  (Table S1).”

### **3. Geographic terminology**

The “Western Mediterranean” is a rather large geographic entity; “continental/regional background” are not unique identifiers of locations. “WMB”, “WMB continental background” and “WMB regional background” (e.g. p.16010, lines 18 and 25, p.16013 line 22) are therefore inexact terms to describe the study sites. For clarity, the authors should refer to the study sites consistently as “MSC” and “MSY” (or “continental/regional background site”), and only use the terms “continental background” and “regional background” when describing results or effects that are generally applicable to a continental or regional background aerosol.

As suggested, the study sites are now identified as MSC and MSY and as continental/regional background site in the whole manuscript.

### **4. PM10 vs. PM1**

The authors should also be specific which PM they are discussing in every piece of text, PM10 or PM1. Sometimes, “PM” trends are discussed that really only apply to one of the two (e.g. p. 16018, line 25).

The authors acknowledge the importance of specifying which PM is being discussed, for this reason we substituted PM for  $\text{PM}_x$  when we refer to both  $\text{PM}_1$  and  $\text{PM}_{10}$  fractions.

### **5. Language**

The writing is generally good, but there are some grammatical and vocabulary errors that could easily be eliminated if the paper were proofread once more.

**Examples:**

**Abstract line 6: “Differences on”,**

The text has been changed as follows:

“Differences in...”

**Introduction line 3: “is of keen current scientific interest”**

The text has been changed as follows:

“The influence of atmospheric particulate matter (PM) on the Earth’s radiative budget generates a strong scientific interest because of its effect on climate.”

**Introduction line 17: “Despite there is not an established definition...”**

The text has been changed as follows:

“Although there is not a well-established definition ...”

**p. 16016 line 9: “and due to a lesser competence with ammonium sulfate”**

The text has been changed as follows:

“... due to a lesser competition with ammonium sulfate formation.”

**p. 16019 line 1: “being the PM1 concentrations...”**

The text has been changed as follows:

“... while the concentrations in PM<sub>1</sub> were very low at both sites...”

**p. 16020 line 1: “opposite to”**

The text has been changed as follows:

“Contrary to ...”

### **Specific comments:**

#### **Section 1:**

**p. 16003, line 6: “Aerosols also have adverse effects in quality” – this is very well established.**

The text has been changed as follows:

“Aerosols also have adverse effects on air quality”

**Line 25: “high altitude or FT environments”:** If a site is over 1000 m in elevation, it does not automatically mean that it is a FT environment, as implied in this sentence. This depends crucially on factors such as the altitude of the surrounding terrain. FT conditions need to be tested for each site.

The authors agree that FT environments depend on surrounding terrain, for this reason the text has been changed as follows:

“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).”

**Line 27: sufficient for what?**

Sufficient to avoid direct anthropogenic emissions.

**p. 16004 line 15: Please provide a reference.**

References have been included in the revised version of the manuscript as follows:

“...since it is in the PM<sub>1</sub> fraction where most of the anthropogenic constituents are concentrated (Minguillón et al., 2012; Pérez et al., 2008b).”

**Line 24: what were the main results of that study?**

The main results of that study were:

“The concentrations of carbonaceous and ionic aerosol follow a typical seasonal trend, with maxima during summer and minima during winter. The average PM<sub>1</sub> mass apportioned by the chemical analyses ranged between  $1.2 \pm 0.68 \mu\text{g m}^{-3}$  (winter) and  $5.0 \pm 2.7 \mu\text{g m}^{-3}$  (summer), with ca. 80% and 60%, respectively, accounted for by organic matter, mainly water-soluble (yearly average WSOC/TC ratio  $0.67 \pm 0.18$ ), the remainder taking the form of ammonium salts. The fine fraction turned out to be mostly neutralized by ammonia, with a slight tendency to acidity during colder months.

This seasonal cycle can be explained by the interplay between the local/mesoscale (vertical) and large-scale (advective) circulations. From mid-spring to late summer, stable anticyclonic conditions and increased turbulent mixing in the lower troposphere, associated to the thermal mountain wind system, induce convective/thermal uplift of air masses from the Po Valley to CMN, strongly altering the free tropospheric aerosol features. Conversely, higher vertical stability at the low levels and variable transport patterns related to the passage of synoptic disturbances over

Northern Italy, determine a weaker influence of vertical transport of pollution on aerosol composition, during midfall-winter.

At CMN, the synoptic-scale circulation regimes presented four principal contributions: Mediterranean, Western Europe, continental Europe and Eastern Europe.”

## **Section 2.2:**

**p. 16007 line 21: Was the same factor applied to the (not high-mountain) MSY site?**

The factor applied to obtain OM from OC was different for each site. It has been included in the new version of the manuscript as follows:

“... organic matter (OM) obtained applying a 2.2 factor to the OC concentrations for MSC samples and a 2.1 factor for MSY samples, following the suggestion from Takahama et al. (2011).”

**line 12: “nss Na concentrations are negligible”: has this been tested in any way?**

The Na concentrations at MSC showed higher values for NAF scenarios. This variation cannot be explained by a higher sea salt contribution during these NAF scenarios and hence it is deduced that a part of the Na is apportioned by the mineral matter. For this reason authors attributed part of the Na to mineral matter, calculated based on typical mineral composition as described in the text. However, at MSY sea salt has been calculated in previous studies as Na+Cl<sup>-</sup>, and the authors think that it is better to keep this calculation in the present study for coherence. To clarify this, the text has been changed as follows:

“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).”

## **Section 3.1:**

**Ripoll et al., 2014 are cited extensively in this section; at times, it is not clear what is a result of his study or a recap of Ripoll et al., 2014 (e.g. p. 16009, line 24, and p. 16010, lines 7 – 14 discussing daily and weekly variations that are not otherwise subject of this paper). This could be clarified by dedicating a separate paragraph explicitly to the summary of relevant results by Ripoll et al.,**

**2014. This section should be clearly separated from the new results of the present paper.**

The authors agree that the results from Ripoll et al., 2014 and the results from the present paper were a bit mixed. Moreover, daily and weekly variations are not the aim of the present study and therefore we have eliminated the paragraph explaining them. This also helped to shorten the paper.

**p. 16009, Lines 5-7: are these differences statistically significant? What are the standard deviations?**

As mentioned earlier, the standard deviations have been included in the new version as follows:

“PM<sub>10</sub> and PM<sub>1</sub> average concentrations ( $\pm$  standard deviation) measured at MSC continental background site reached  $11.5 \pm 9.3 \mu\text{g m}^{-3}$  and  $7.1 \pm 3.9 \mu\text{g m}^{-3}$ , respectively, whereas at MSY regional background site these concentrations were  $15.5 \pm 7.9 \mu\text{g m}^{-3}$  and  $8.2 \pm 4.1 \mu\text{g m}^{-3}$  (Table S1).”

**“Warmer months”, “colder months” (e.g. line 18): please define which months constitute the “warmer” and “colder months”.**

This sentence has been moved to section 3.4 and modified as follows:

“In the warmer months (April-September) the development of the PBL at MSC... On the other hand, in the colder months (October-March) the lower vertical development...”

**Line 14: how low? It would be nice to have an average, or at least example PM10 and PM1 concentrations for the free tropospheric conditions, as the annual averages reported (11.5 and 7.1) are averages of FT and BL values.**

The concentrations under free tropospheric conditions should be very similar to the concentrations during winter, as MSC is located in the FT on most days during this season. The old Figure 1 and the new Figure 3 shows the average concentrations of aerosol major components in PM<sub>1</sub> and PM<sub>1-10</sub> during winter.

The limitations in the estimation of the PBL height led us to decide not to include such an average concentration (within BL and within FT averages). As explained later, the overall variation of the PBL height is valid and it helps in the

interpretation of results, but trusting every single point individually could lead to wrong averages.

**Line 20: “higher convection”: is this based on the modeled BL development? What is the significance of forestation to convection?**

This sentence has been moved to section 3.4 and modified as follows:

“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 (Rodríguez et al., 2002), and to the higher cooling effect from the sea breeze at the regional background sites.”

**Line 22: “higher PBL development”: what exactly is meant by that? If the PBL gets higher at MSC, will it not transport pollutants up to the site, causing, if anything, an increase in PM concentrations?**

As this sentence was confusing, the authors decided to eliminate it.

**Line 24: Why are Ripoll et al., 2014, cited here? Should this not emerge from the dataset presented in this study?**

This sentence has been modified in the new version of the manuscript as follows:

“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).”

**Line 24: “This has been concluded for”: “Similar trends have been observed at” would be better.**

It has been changed as pointed in the previous comment.

**p. 16010, Line 7: “However,”: This qualifier is not needed, as no one would expect PM<sub>1</sub> to be driven by the dust suspension discussed in the previous sentence.**

This paragraph has been eliminated.

**Line 22: “Saharan dust particles” are cited as a reason for “higher PM” concentrations at MSC compared to Puy de Dome and Jungfrauoch: Please specify: PM<sub>1</sub> or PM<sub>10</sub>? In the long-term average, or episodically? It would be surprising if dust particles are the reason for higher PM<sub>1</sub> concentrations. Geographical differences could be responsible, too, at the very least for the comparison with Jungfrauoch, which likely spends more time in the free troposphere than MSC, due to its much higher altitude.**

This phrase has been modified in the revised version of the manuscript as follows:

“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 Jungfrauoch at 3454 m a.s.l. in Switzerland (Cozic et al., 2008), shows that PM<sub>10</sub> and PM<sub>1</sub> concentrations were higher at the continental background site in the WMB (Fig. S3 and Table S1). Such higher PM<sub>10</sub> and PM<sub>1</sub> 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).”

Moreover, the impact of NAF episodes on PM<sub>1</sub> concentrations has been included in section 3.3.1 (North African episodes) as follows:

“The PM<sub>1</sub> non-NAF to NAF increase was attributed to the increment of PM<sub>1</sub> MM, sulfate, nitrate, ammonium, OM, and EC (Figs. S5 and S6). In relative contribution the highest difference in PM<sub>1</sub> concentrations was recorded for MM at MSC (Fig. 4) thus evidencing that NAF episodes also affect the fine fraction.”

### **Section 3.2:**

**p. 16011, Line 3: “On average”: average over what?**

The average values shown in the whole paper are the average over the whole study period (January 2010-March 2013) unless otherwise specified (e.g. averages for

atmospheric episodes), as it is written in the figure captions. Nevertheless, in the new version of the manuscript, this particular “On average” has been eliminated as follows:

“PM<sub>1</sub> 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<sub>1-10</sub> 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<sub>1</sub> fraction points to the suitability of using PM<sub>1</sub> as indicator of regional anthropogenic pollution in Europe, and reflects the wider spatial representativeness of the fine PM.”

**Line 4 and following: The values in brackets should be written as “(17 and 21%)” as they could otherwise be misinterpreted as a range of measurements, rather than two averages for the two sites. In line 6, the two average undetermined mass values for the two sites should not be described as “ranging between”, as they are not a range of measured values.**

All these suggestions have been included in the revised version of the manuscript as can be seen in the previous comment.

**Line 9: “Absolute concentrations” should be discussed in Section 3.1.**

The absolute concentrations are now discussed in section 3.2.1 (Average aerosol chemical composition).

**Section 3.2.1:**

**Line 23: please specify the time period of the average in the text.**

As mentioned earlier, the average values shown in the whole paper are the average over the whole study period (January 2010-March 2013) unless otherwise specified (e.g. averages for atmospheric episodes), as it is written in the figure captions and tables.

**Line 26: “size distribution” is the more commonly used term (several instances in the paper)**

The authors do not well understand what the reviewer is making reference to with this comment. The referenced line has been revised and it is correct with our criteria.

**Line 27: “nitrate compounds were associated”...how was this determined?**

It is very well known that coarse nitrate is formed from the reaction of nitric acid and/or some other nitrogen compounds with mineral dust and sea salt particles (Wall et al., 1988; Zhuang et al., 1999a).

**p. 16012, line 11: It seems that the maxima in February-April and October at MSC could also be a combination of BL effects and the mentioned volatility: the free troposphere episodes at MSC decrease overall mass concentrations in winter, the warmer temperatures specifically decrease nitrate concentrations in summer, in the transition months, neither of the two processes are effective.**

This discussion has been moved to section 3.4 (seasonal variation of continental and regional background aerosol chemical composition) and has been changed as follows:

“**Nitrate** concentrations decreased in summer at both sites, especially in PM<sub>1</sub> (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.”

**Line 19 and following: In Figure 3, NAF, AN and EU show similarly high nitrate concentrations. WREG showing the highest concentrations is an observation not repeated in any other constituent, which is why pollution episodes may not be the only explanation (for pollution episodes, I would expect the trend to be repeated in EC, for example). Since WREG is a class limited to winter months, it seems that the low temperatures may be part of the reason for the increased nitrate concentrations, compared to the other air mass classes**

**(and in particular compared to the low SREG concentrations). The high concentrations during NAF are interesting, since NAF are more frequent in summer, yet nitrate concentrations are very high.**

The NAF episodes are now explained in section 3.3.1 (North African episodes (NAF)) including the high nitrate concentrations as follows:

“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<sub>1</sub> and PM<sub>1-10</sub> can be related to the interaction of dust with anthropogenic pollutants.”

**p. 16013, line 4: “air mass from mainland Europe” – please add the abbreviation EU.**

It has been changed as follows:

“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.”

**line 7: do you mean Eastern Europe is “one of the most polluted regions”, or do you mean both of them? Please provide a reference.**

This discussion has been moved to section 3.3.4 (European episodes (EU)) and has been changed as follows:

“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).”

**Line 9: how does the fact that EU air masses are more frequent in February – April and in October impact the average calculated for nitrate? There is an overlap here with the annual cycle of nitrate concentrations at MSC, which, as outlined before, may have its origins in local effects, as well.**

The authors agree that the origin of nitrate can be influenced by different factors. But in this particular region what we observed is that high concentrations of nitrate were measured in the colder months, however they were not measured simultaneously at MSC and MSY (old Figure 2 and new Figure 6), as it is the case of sulfate. Moreover, average concentrations of nitrate as a function of atmospheric episodes (old Figure 3 and new Figure S5) shown that the higher concentrations of nitrate at MSC were measured under EU episodes. Therefore, high nitrate concentrations at MSC and MSY during the colder months have different or partially different origin. If the nitrate had a local/regional origin it will be more similar at both sites and it is not the case.

### **Section 3.2.2:**

**p. 16014, line 8: “was associated with” – “was attributed to” would be better, unless it has been somehow confirmed.**

The text has been changed as follows:

“Nevertheless, PM<sub>1-10</sub> sulfate was also detected at MSC and MSY, and it was partially attributed to mineral dust...”

**Line 11: The seasonal cycles are similar in the rough sense stated (higher concentrations in warmer months), but there are differences in the seasonal cycle, especially in PM10 (lower concentrations at MSC in May, June, and July).**

As shown in the old Figure 2 and in the new Figure 6, sulfate concentrations as a function of month had a high dispersion at both sites, but the range of dispersion was similar at both sites. The decrease in May, June and July at MSC could be due to the higher Atlantic advections during these months at MSC (old Figure S5 and new Figure 1), since OM and EC also showed a decrease.

**Line 14: longer residence time compared to what? Given the possibility of wet removal, is that residence time long enough to lead to homogenization across a wide geographic area, as suggested here?**

Sulfate has a longer residence time in the atmosphere than other components. This has been previously studied (Seinfeld and Pandis, 2006). The difference in stability is enough to result in a higher homogeneity of sulfate concentrations, since in

the WMB the precipitation in summer is very scarce. This is what we observe in the present study. Sulfate showed clearly higher similarities between sites than any other component, both in absolute concentrations and in the seasonal variation. The squared Pearson correlation coefficient between the daily sulfate concentrations at MSC and MSY is 0.71, which reflects the high homogeneity of this component.

The following text has been added to the revised manuscript:

“The squared Pearson correlation coefficient between the daily sulfate concentrations at MSC and MSY was 0.71”.

**Line 16: “was linked” – has a causal link been established? Otherwise, it should read “is likely due to”, or something to the effect.**

Text has been changed as follows:

“The summer maximum was likely due to the higher...”

**Line 19: It seems like this compression of the BL would be a general PM trend, and not just specific to sulfate. Figure 4 b) seems to confirm this for MSY.**

This discussion has been moved to section 3.3.1 (North African episodes (NAF)) and has been changed as follows:

“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.”

**p. 16015, line 3: Did you mean the impact of the NAF event was less important? The increase of sulfate concentrations cannot be “important”, it can only be more or less.**

The authors mean that the increase in sulfate concentrations during this particular NAF episode was less noticeable, pronounced, marked in the continental background site. The text has been changed as follows:

“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.”

**Line 3-6 : This would be a good place to look at relative chemical composition rather than absolute values.**

As mentioned earlier, Figure 3 and Figure 6 (now Figure S5 and Figure S6) have been replaced by Figure 4, which show relative chemical composition as a function of atmospheric episode.

**Line 10: It is not clear how an impact of shipping emissions is visible in Figure 3, or which air mass is even talked about. MED? Again, the discussion of absolute concentrations is problematic here: Can the advection of shipping emissions in presumably otherwise relatively clean marine air really lead to an increase of absolute SO<sub>4</sub> concentrations on land? If so, can you provide a reference? The statement is at odds with a statement in the same section (previous page, line 25) stating that the sea breeze has a “clean-up” effect.**

Sulfate emissions in the study region are relatively low compared to other regions with high thermo power plants. Moreover, shipping circulation in the Mediterranean Sea is very high especially during summer, with higher frequency of cruises, as it can be seen with the variation of V concentrations (tracer of shipping emissions (Minguillón et al., 2014; Pey et al., 2013)). Consequently the increase in sulfate concentrations during summer was partially attributed to shipping emissions. To clarify this discussion, the text has been changed as follows:

“Additionally, regional background sulfate aerosols in summer could be affected by the transport of shipping emissions from the Mediterranean to the continental areas...”

### **Section 3.2.3:**

**p. 16016, line 5: the “colder months” were never specified, so it is unclear what the “rest” of them are, after November – January.**

As mentioned earlier, warmer and colder months are now specified in the text, and for this particular discussion the months have been included as follows:

“Nevertheless, at MSC lower ammonium concentrations in November-January were recorded, as MSC is mostly within the FT in this period. During the rest of the colder months (October, February and March) at MSC, and in the whole colder period at MSY...”

**Line 20: “sporadically high values” are not shown in Figure 3. WREG seems to be associated with moderate sulfate concentrations there.**

In the revised version of the manuscript it has been referred to the old Figure 4 which is now Figure 5.

**Line 14: Shouldn't this show in a similar seasonal cycle of NH<sub>4</sub> and SO<sub>4</sub> at MSY? This does not seem to be the case (Figure 2).**

The ammonium seasonal variation discussion has been moved to section 3.4 and has been changed as follows:

“**Ammonium** concentrations did not follow a clear seasonal pattern (Fig. 6) due to its association with both sulfate and nitrate.”

**p. 16017, line 2: “was linked to”: was a causal link established?**

The text has been changed as follows:

“The summer maximum was due to...”

**Lines 2 – 5: These processes are all plausible, but if there was no actual causal link established, the authors should rather say “may be linked to”. Concerning the annual cycle of PM at the two sites: Since absolute concentrations are what's discussed, why is there no mention of boundary layer effects as a driver for absolute concentrations (especially in winter) at MSC? This is another example for where relative contributions may be more enlightening.**

This discussion is now in section 3.4 (seasonal variation of continental and regional background aerosol chemical composition) and has been changed as follows:

“**Organic matter** concentrations followed a similar seasonal variation at both sites, with the highest values during the warmer months (1.8 and 1.5 times higher than the winter concentrations at MSC and MSY, respectively) (Fig. 6). The summer maximum was due to: 1) the higher temperature and photochemistry in the atmosphere that enhances the formation of SOA; 2) the accumulation of pollutants over the WMB owing to the occurrence of SREG and NAF episodes; 3) the greater biogenic emissions from vegetation (Seco et al., 2011); and 4) the higher frequency of wildfires. Furthermore, at MSY a secondary maximum of OM concentrations occurred in

October-March linked to the occurrence of WREG episodes. The continental background site was less affected by this type of episodes, since MSC is mostly within the FT in winter.”

**Line 6: This sentence is confusing. Which of “these processes” are relevant to NAF? Shouldn’t NAF (along with MED) be mentioned in point (2) in the previous sentence, as they, too, are more prevalent in summer and associated with high OM concentrations?**

The authors agree that this sentence is confusing, so we have eliminated it.

**Line 20: According to Figure 3, it was detected in almost all air masses at MSC.**

This discussion is now in section 3.2.2 (Partitioning of major and trace components in  $PM_1$  and  $PM_{1-10}$ ) and the text has been changed as follows:

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

**p. 16018, line 3: BL effects could be important here, too.**

The PBL effect is now discussed in section 3.4 (seasonal variation of continental and regional background aerosol chemical composition).

**Line 10: see my comment on shipping emissions above.**

See the answer above.

#### **Section 3.2.6:**

**p. 16019, line 11: “Furthermore” is a confusing transition from the long-range dust transport topic to the local dust source topic. Perhaps something like “But local dust can be important, as well: ...”?**

This is discussed in section 3.4 (seasonal variation of continental and regional background aerosol chemical composition) as follows:

**“Mineral matter** concentrations and mineral trace elements in the WMB are driven by the local and regional dust resuspension and by the contribution of African dust outbreaks, both enhanced in the warmer months. Consequently, the highest values were measured in summer and the lowest in winter, with sporadic high concentrations in March-April (Figs. 6 and 7).”

#### **Section 3.2.8:**

**p. 16021 line 16: “contribution to the total mass”:** is that truly a calculated contribution to total mass or is it the order of % variance explained from tables S2 and S3? If it is the latter, it should be called that.

It is the contribution to the total mass, calculated as the sum of absolute concentrations with respect to the mass of PM. As shown in the old and new Figure 7, the group of trace elements whose contribution accounted the more to the total trace elements mass was the mineral, followed by the industrial+road traffic and the lower was the fuel oil combustion group.

**p. 16022, line 2: “enriched”:** It would be better to state the high factor loadings as it was done for the mineral trace elements. “enriched” should be used when talking about actual chemical enrichment of a sample.

This is discussed now in the section 3.2.1 Average aerosol chemical composition. The word enriched does not appear in the manuscript anymore, but high factor loadings are used to explain the associations of the trace elements. The text now reads as follows:

“In the mineral group typical crustal elements (Ti, Mn, Li, and Sr) were included, but also V, Cr, Co, Ni, and As were partially associated with this factor since these elements, usually attributed to anthropogenic sources, are also found in clay mineral assemblages. The group for which high loading factors were obtained for Cu, Zn, As, Cd, Pb, Sb and Sn was associated with industrial + road traffic sources, based on previous studies [...] The fuel oil combustion group was better identified at MSY than at MSC, and it was traced by V and Ni [...].”

#### **Section 4.**

**p. 16024 line 23: “advection”, not “advections”.** Does this refer to a specific air mass class?

The Atlantic advections are the air masses from the Atlantic sector and they are discussed now in section 3.35 (Atlantic advections (AN, ANW, ASW)).

**p. 16025 line 8: This sentence gives the impression that “time variation” was directly studied (which it was not, except for the short case studies), and that the meteorological variables mentioned here were part of the data analysis presented in this paper (which they were not).**

The authors agree that this sentence is confusing, so we have eliminated it.

**Line 8: relatively high compared to what?**

Compared to other European sites as reported in the present study.

**Line 11: “the importance of atmospheric processes resulting in a complex vertical distribution with a wide horizontal representativeness” This is a rather vague statement and it is not clear how it emerges as a conclusion from the paper.**

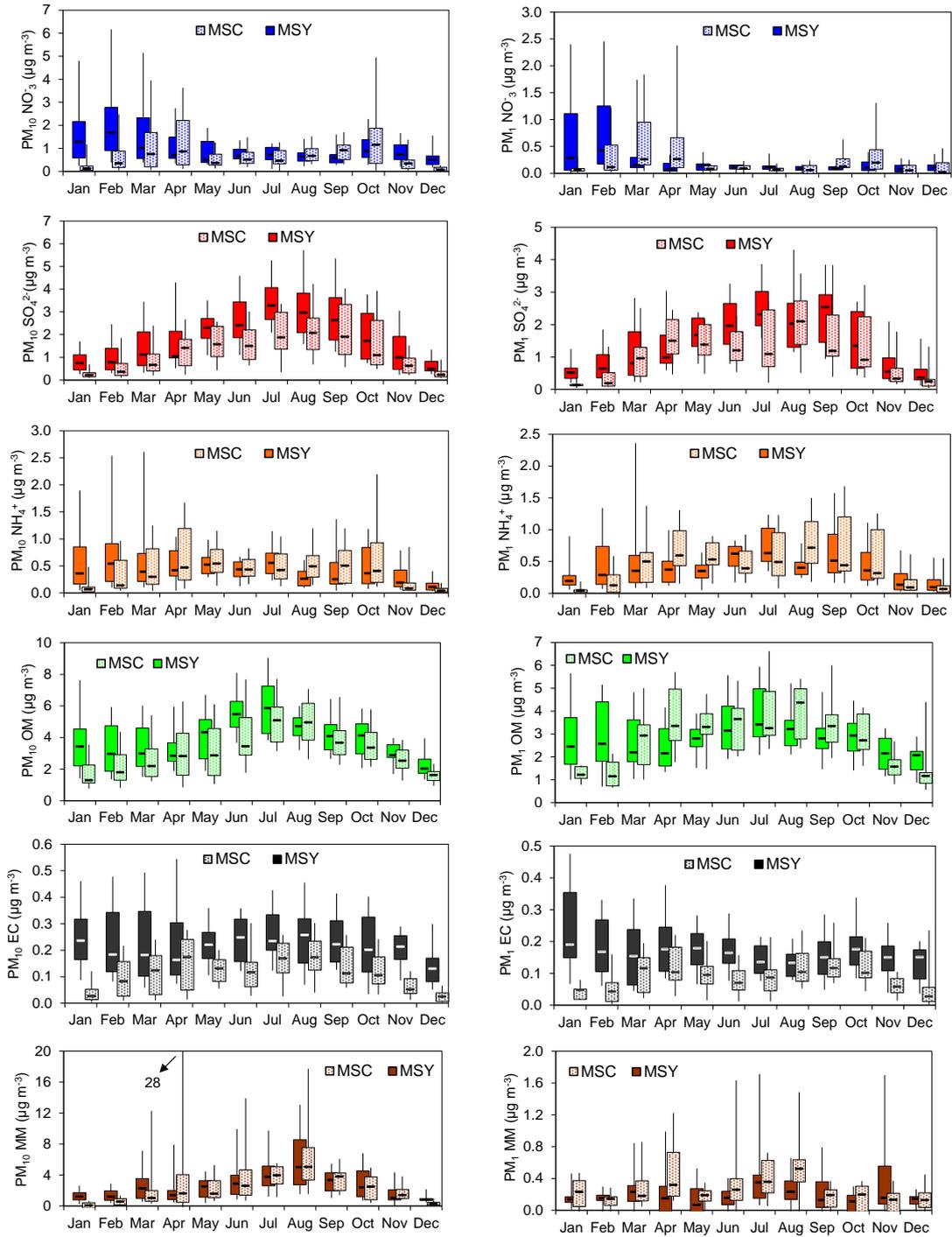
The text has been changed as follows:

“...taking into account the importance of atmospheric processes.”

**Figures:**

**Figure 2: It would be easier to compare the two sites if MSC and MSY were put on the same plot, with PM1 as the left column and PM10 as the right column.**

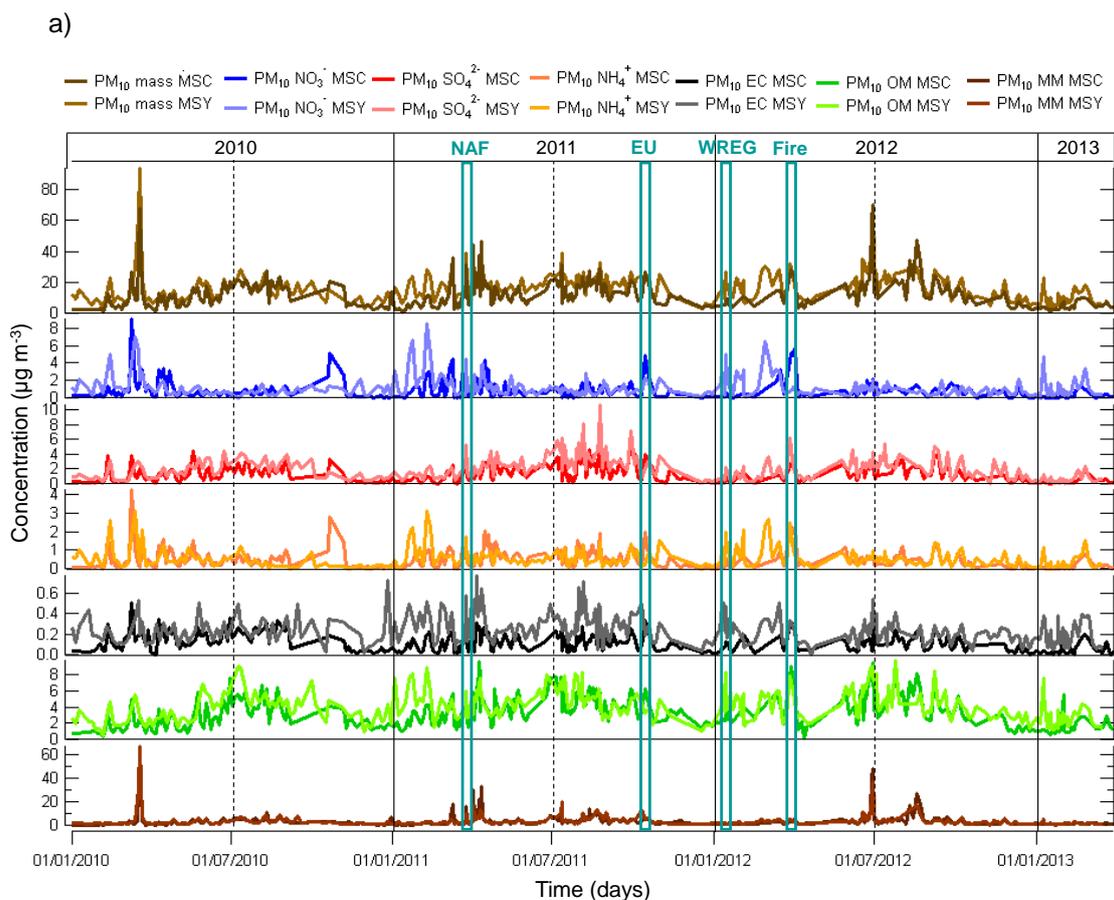
The authors agree and the old Figure 2, which is now Figure 6, has been changed as follows:

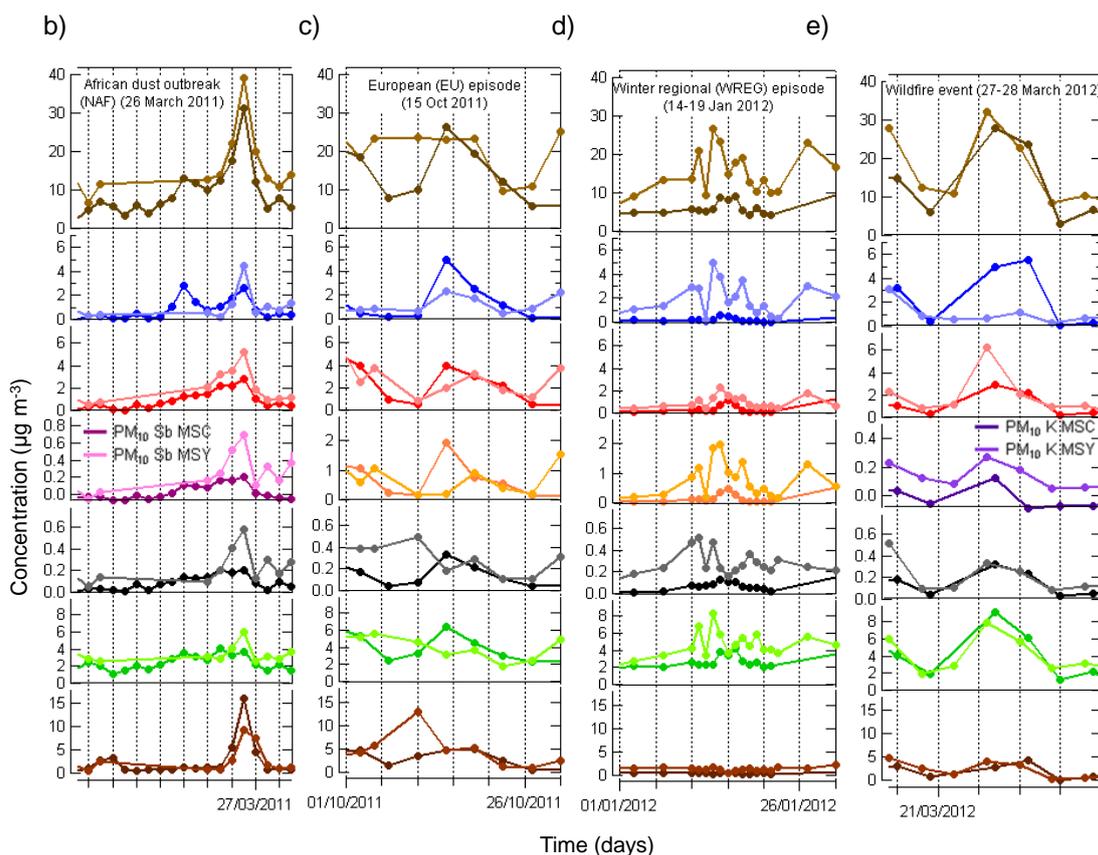


**Fig. 6 Monthly median (black line within the boxes) and percentiles (5-25-75-95, boxes and whiskers) of major  $PM_{10}$  and  $PM_1$  chemical components concentrations at Montsec (MSC) and Montseny (MSY) based on daily measurements between January 2010 and March 2013.**

**Figure 4:** The text in this figure is too small, it is impossible to read when printed. The readability of this figure would be greatly enhanced if the legend were spaced out, or split up, such that the legend entry for the two graphs in each plot is next to (or in the top right corner of) that plot. It is currently very hard to color-match the legend entries to the graphs.

The authors agree and the old Figure 4, which is now Figure 5, has been changed as follows:





**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) winter regional episode, and (e) wildfire event, with daily  $PM_{10}$  mass and  $PM_{10}$  chemical components concentrations.

**Figure 5:** it would be better to split this figure into several, with different axes, to avoid the log-scale, which makes it hard to see the differences between the sites.

The authors acknowledge the possible difficulty of seeing the values of this figure, for this reason we included the Table 1 with all the values and preferred to keep the old Figure 4, which is now Figure S3, as a single figure in order to not increment the number of figures.

**Figure S3:** How representative are these model calculations for the actual local BL development at the stations? BL development, particularly in mountainous regions and with respect to aerosol transport, is a local process, governed by the local topography at a scale below the resolution of many

**models. What grid resolution was the HYSPLIT model run on? Has the BL development at MSC and MSY been studied in terms of local measurements (local meteorological parameters, soundings, tracers, etc.)?**

The authors are aware of the limitations of PBL height estimates based on READY model. This model uses a 50 km resolution grid. Since this horizontal resolution is not very good for mountain regions such as MSC (1000 m peak in just 20 kms) and MSY (Fig. S1 bottom), the estimate average terrain height from the model is around 580 m and 400 m for MSC and MSY, respectively, whereas the real altitude of these sites is 1570 m and 750 m. Furthermore, the model gives only the PBL height every three hours and we assumed that the PBL height does not change during the next three hours after the datapoint. These limitations have to be considered when analyzing the data as a function of the PBL height. To include these limitations in the revised version of the manuscript, the following text has been added:

“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.”

**Technical corrections:**

**p. 16004 line 11: “they mostly correspond to”: “they were mostly taken in” would be better.**

The text has been changed as follows:

“Most studies focusing on PM<sub>1</sub> 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...”

**p. 16003, Line 14: “determine” would be better than “define”**

The text has been changed as follows:

“For this reason, measurements performed at a sufficient distance from large emission sources are needed to determine background conditions...”

**p. 16003, Line 18: “considered”: “described as” would be better**

The text has been changed as follows:

“Despite the fact that there is not an established definition, continental background environments can be described as representative of the air quality...”

**p. 16008 line 1: “given by” should be “calculated as”**

The text has been changed as follows:

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

**p. 16012, Line 15: “maximum nitrate concentrations” or “maxima in nitrate concentrations”**

The revised version of the manuscript described the nitrate seasonal variation as follows:

“During the colder months higher nitrate concentrations...”

**p. 16015, line 4: “since these reached”: “reaching” would be better.**

The new version of the manuscript described the NAF example as follows:

“On the other hand, the associated compression of the PBL was reflected in the PM<sub>10</sub> sulfate concentration from 26 March 2011 at MSY, which reached 5.2 µg m<sup>-3</sup> ...”

**p. 16017, line 24: “latest” should be “latter”**

The paragraph has been moved to section 3.2.2 and the sentence has been eliminated in the revised version of the manuscript.

**p. 16019, line 1 and line 18: grammar needs to be corrected.**

The text has been changed as follows:

“As expected, most of the **MM** species and the mineral trace elements were encountered in the PM<sub>1-10</sub> fraction, while the concentrations in PM<sub>1</sub> were very low at both sites (Figs. 3 and S6 and Table S1).”

“...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.”

**p. 16023 line 21: “has been estimated in” should be “was estimated to be”**

The text has been changed as follows:

“In this particular region of the WMB, the continental to regional background increase was estimated to be  $4.0 \mu\text{g m}^{-3}$  for  $\text{PM}_{10\dots}$ ”

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