

Impact of aerosol sources on optical properties at urban, regional and continental levels in the north-western Mediterranean

The authors would like to thank the reviewers for their comments and suggestions, which helped improving the quality of this work. A new version of the manuscript has been prepared following the referee's suggestions. We provide below detailed replies to each of the comments.

Anonymous referee #1

**Overall Quality/General Comments:** The primary objective of the paper is to quantify the mass scattering and absorption efficiencies (MSE and MAE) of different aerosol source types observed at urban (Barcelona-BCN; MAE only), regional background (Montseny-MSY), and remote background (Montsec-MSA) sites in the northwestern (NW) Mediterranean region. To accomplish this, the authors applied a multi-linear regression model (MLR; Eqs. 1 and 2) to a ~4-year time series of aerosol source type mass concentrations (derived using PMF), PM10 aerosol light scattering and absorption coefficients ( $\sigma_{sp}$  and  $\sigma_{ap}$ ). The aerosol source mass concentrations served as dependent variables and the  $\sigma_{sp}$  and  $\sigma_{ap}$  served as independent variables. Note that I am using the common symbols  $\sigma_{sp}$  and  $\sigma_{ap}$  as shorthand for the coefficients. The authors did not use these symbols. The combined PMF/MLR approach yields more useful MSE and MAE for source apportionment studies, since they are given in terms of aerosol source types instead of chemical components. Armed with the SAE and MAE for each of the observed aerosol source types, the authors calculated the  $\sigma_{sp}$  and  $\sigma_{ap}$  contributions for each source type and summed the contributions to yield total calculated  $\sigma_{sp}$  and  $\sigma_{ap}$ . They then compared these calculated coefficients with measured  $\sigma_{sp}$  and  $\sigma_{ap}$  (at RH $\leq$ 40%) over the period (2010-2014 at BCN and MSY; 2011-2014 MSA) during which aerosol optical properties and composition were simultaneously measured. They used good agreement in this comparison to validate their source specific SAE and MAE. They then used the source-specific SAE and MAE along with measured composition to reconstruct  $\sigma_{sp}$  and  $\sigma_{ap}$  for pre-2010, when there were only mass concentration measurements (i.e. no  $\sigma_{sp}$  and  $\sigma_{ap}$  measurements). The reconstructed from  $\sigma_{sp}$  and  $\sigma_{ap}$  was merged with the measured values from 2010-2014 at MSY in a trend analysis. The combined PFM//MLR technique could find use in other source apportionment studies and the derived MAE and MSE for the individual aerosol sources also find potential use in the modeling community (although I am not a modeler) and possibly in regional pollution mitigation strategies. However, I believe that serious issues regarding scientific quality and presentation quality must be fixed before this manuscript is acceptable for publication. These issues are described in the broad and specific comments below. **Scientific Significance:** The perceived significance lies in the fact that the authors derived MSE and MAE for the various aerosol source types, instead of doing so for speciated mass concentrations. The PFM/MLR technique yielding source-specific MSE and MAE is novel (to the best of my knowledge) and the results of Sect(s). 3.1-3.4 could contribute to improved knowledge of source-apportioned contributions to aerosol light scattering and absorption coefficients over the 2010-2014 period at the 3 NW Mediterranean sites (minus the MAE at BCN). The utility of the reconstructed  $\sigma_{sp}$  and  $\sigma_{ap}$ , and single-scattering albedo (SSA) for pre-2010 (Sect. 3.5) and the resulting trend studies (Sect.3.6) is questionable-in my opinion. See my comments below regarding Scientific Quality. I would rate the Scientific

Significance as 'good' if the authors focus on the results of Sect(s). 3.1-3.4 and improve upon the Scientific Quality.

**Reviewer#1. General comment 1. Scientific Quality:** I rate the scientific quality as 'fair'. I am not an expert on PMF but the scientific approach and applied methods seem acceptable, up until Sect. 3.5- Reconstruction of scattering, absorption, and SSA time series. In Sect. 3.5, the authors discuss strong correlations between the measured and calculated aerosol  $\sigma_{sp}$ ,  $\sigma_{ap}$ , and SSA for the period 2010-2014 at BCN and MSY, and for the period 2011-2014 at MSA, when the optical property measurements are available (Fig. 4). They state (bottom of P.16) that "As a result, long-term time series of scattering and absorption were satisfactory reconstructed when chemical data was available, for the period 2004- 2014 at BCN and MSY and for the period 2011-2014 at MSA (Fig. 6)." However, high correlation and good agreement between measured and calculated scattering and absorption coefficients is to be expected, since the source-specific MSE and MAE are being evaluated using the same dataset that was used to determine them (via the MLR). The authors could (should?) have used different subsets of the period to test the model than that used to develop the model.

Authors agree with the referee, independent datasets of source mass contributions together with the obtained source specific MSE/MAE, should have been used to reconstruct scattering ( $\sigma_{sp}$ ) and absorption ( $\sigma_{ap}$ ) coefficients for a different period not used in the MLR analysis.

This analysis was not performed in the initial version of the manuscript due to the limited availability of chemical analysis results for ions concentration ( $Cl^-$ ,  $NO_3^-$ ,  $SO_4^{2-}$ ) for the year 2015.

In the revised paper we present reconstructed time series of  $\sigma_{sp}$  and  $\sigma_{ap}$  for the year 2015 at MSY. With this aim, a new PMF was performed for the period 2004-2015. Then, the resulting PMF source contributions obtained for the period January-December 2015 were used together with the corresponding MSE and MAE, previously obtained by means of the MLR model for the period 2010-2014, in order to compute  $\sigma_{sp}$  and  $\sigma_{ap}$  coefficients for the year 2015.

This analysis provides an insight on the capability of the PMF-MLR technique to estimate  $\sigma_{sp}$  and  $\sigma_{ap}$  coefficients for those periods when optical properties measurements are not available.

Following the Referee's suggestion, section 3.5 of the revised manuscript contains the evaluation of the PMF-MLR technique using independent datasets of chemical source contributions for the year 2015. The following paragraph has been added to the revised paper:

"An independent subset of the study period was considered, in order to further evaluate the PMF-MLR technique and the accuracy of the method to simulate optical properties when chemical source contributions were available. Therefore, a new PMF was performed in order to obtain the source contributions for the period 2004-2015 at MSY. With this aim, the simulation of  $\sigma_{sp}$  and  $\sigma_{ap}$  coefficients for the period January-December 2015 was carried out by means of the source specific MSE and MAE previously obtained in the MLR analysis for the period 2010-2014. Good agreement was found between modeled and measured  $\sigma_{sp}$  ( $R^2=0.85$ ) and  $\sigma_{ap}$  ( $R^2=0.76$ ) coefficients, at 525 and 637 nm respectively, showing slopes close to one for the year 2015 at MSY (Fig. 6). This analysis confirms the confidence of the PMF-MLR technique to accurately estimate  $\sigma_{sp}$  and  $\sigma_{ap}$  coefficients when chemical data is available."

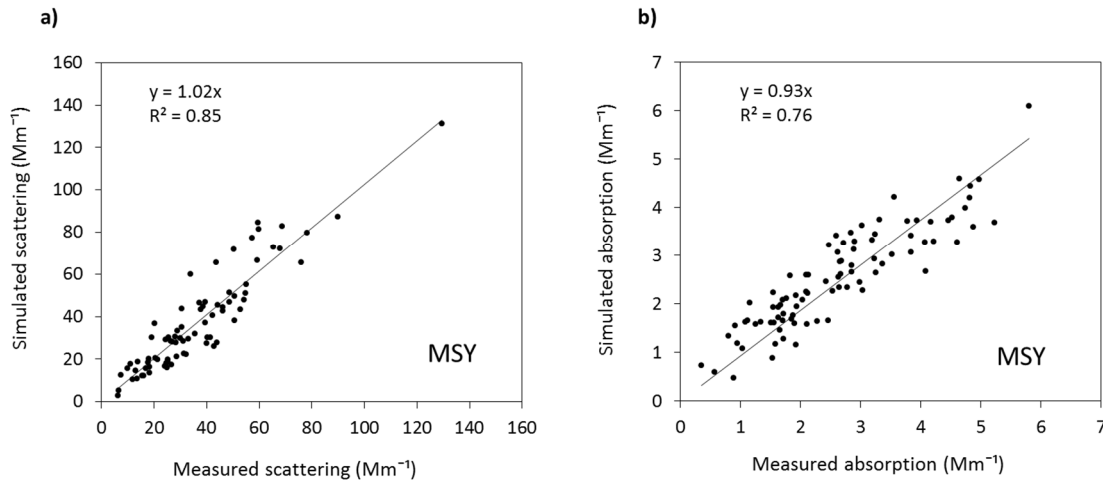


Figure 5. Relationship between measured and modeled (a) scattering at 525 nm and (b) absorption at 637 nm at MSY for the period January 2015–December 2015.

**Reviewer#1. General comment 2). The utility of the reconstructed SSA is highly questionable. In addition to the issue that I just discussed, the agreement between measured and calculated SSA was marginal during the 2010–2014 period at MSY ( $R^2=0.42$ ; slope=0.80). This marginal agreement does not inspire confidence that the reconstructed SSA is sufficiently accurate for use in any trend studies (Sect. 3.6), much less the assertions made by the authors regarding the results from this trend study. There are also many cases where the claims made by the authors are not supported by the available data (See my specific comments below) or references to the sources of claims made by the authors are not given.**

Following the referee's comment, the SSA trend analysis has been removed from section 3.6. Results making reference to this part of the paper have also been removed from the conclusions section. Modifications are directly shown in the revised manuscript.

**Reviewer#1. General comment 3). Presentation Quality: This is the major weakness of the paper and requires significant improvement before the paper is acceptable for publication. I would rate this as 'poor' for the current version of the manuscript. My major criticisms are related to grammar and (to a lesser degree) structure of some paper sections (mainly the Introduction). The manuscript is full of long, rambling sentences with incorrect punctuation (ex: missing commas), misspellings, and improper usage of tenses. The first paragraph of the Introduction section is a good example of the above-mentioned grammatical errors but they pervade throughout the paper. The grammar also limited my ability to understand some of the authors' interpretation of results. In several places, the wording likely does not convey their meaning (see specific comments**

for a few examples). There are way too many grammatical errors for me to list in my specific comments and doing so detracts my focus from the other aspects of the paper. I strongly encourage the authors to have someone (colleague or an English editor) carefully look over the document for grammar and fix this. Then have the same colleague or someone else carefully evaluate the grammar of the revised manuscript. Related to grammar is the inconsistent use of tenses. Past and present tenses are used interchangeably when describing methods and results reported by others. Past tense should be consistently used to describe previous studies and present tense is typically used to describe the current study. Please fix this throughout the manuscript. The structure of Introduction section should also be modified to improve readability and a few figures require improvements (See my specific comments below regarding these issues). In summary, I would rate the current version of the manuscript as 'fair'.

Following the Referee's suggestions regarding presentation quality of the manuscript, grammatical aspects of the discussion paper have been revised for a better understanding. Particular attention has been paid to the proper use of tenses and the structure of the introduction section. Changes have been directly modified in the discussion paper.

**Specific Comments and Technical Corrections:** Note that there are too many grammatical issues for me to list so I only listed a few. Please have a colleague review the manuscript very carefully for grammar and then fix.

**Reviewer#1. Specific comment 1).** The abstract is too long and should be shortened.

The abstract has been shortened from 574 to 453 words. Modifications are directly included in the revised manuscript.

**Reviewer#1. Specific comment 2).** Readability of the Introduction section would be much improved if the authors arranged it in the following order: (1) Statement of the problem-Why is knowledge of MAE and MSE important? (2) Results from previous works; (3) How this study will advance knowledge and what is unique about it? These are all included in the existing version of the Introduction but are mixed, long-winded, and the section does not read well. Significantly reduce description of methods (both those of others and the current study) to only that necessary to accomplish (1)-(3) and save any more details for the Methodology section.

The introduction section has been rephrased. Modifications have been directly added to the revised manuscript.



**Reviewer#1. Specific comment 3). P.3 Lines 26-32: The wording of temporal and spatial aerosol variability and the reasons for this variability is repetitive and this 7-line passage could be condensed into ~3 lines.**

The paragraph has been shortened from 128 to 71 words:

"However, a thorough quantification of the direct and indirect aerosol effects on the Earth's radiative budget is difficult to achieve (Zieger et al., 2012). The high spatial and temporal variability of atmospheric aerosols along with the large differences in particle composition and size (Andrews et al., 2011; Bond et al., 2013; Haywood et al., 1999), results in a changing radiative forcing from local to global scales (Collaud Coen et al., 2013)."

**Reviewer#1. Specific comment 4. P.4 Line 1: "The determination of MSE and MAE for specific aerosol components has been subject of research in the last few years." It has been the subject of research for more than the last few years so this sentence should be reworded or omitted. My suggestion is to omit it, as it is vague and really does not add much to the paragraph.**

Following the referee's suggestion, the sentence has been removed from the revised manuscript.

**Reviewer#1. Specific comment 5. P.6 Lines 19-24: "The three sites are involved in the Catalanian air quality monitoring network. Additionally, the MSY and MSA stations form part of the ACTRIS (Aerosol, Clouds and Trace gases Research InfraStructure) and GAW (Global Atmosphere Watch) networks, and then aerosol optical measurements were performed following the standards required by these networks." I suggest re-wording as "The three sites are members of the Catalanian air quality monitoring network, ACTRIS (Aerosol, Clouds and Trace gases Research InfraStructure) and GAW (Global Atmosphere Watch). Aerosol optical properties at the sites are measured following standard network protocols". Then include reference(s) describing these protocols.**

It should be noted that the Barcelona site is not a member of the ACTRIS/GAW networks. The sentence has been modified as follows:

"The three sites are members of the Catalanian air quality monitoring network. Additionally, MSY and MSA are part of the ACTRIS (Aerosol, Clouds and Trace gases Research InfraStructure) and GAW (Global Atmosphere Watch) networks. Aerosol optical properties at the sites are measured following standard network protocols (WMO/GAW, 2016)."

The reference corresponding to the GAW standard protocols is cited in the revised manuscript:

"WMO/GAW report 227: Aerosol Measurement Procedures, Guidelines and Recommendations, 2nd Edition, 2016, 103 pp. August 2016 (WMO-No. 1177)."

**Reviewer#1. Specific comment 6. P.7 Line 7: "Samples were collected every 3/4 days". I am confused as to whether this means "3/4 day" or "3 to 4 days". I am assuming that the authors imply the former but then remove the 's' from 'days'. This also illustrates the author' usage of past tense to describe the current study. I recommend consistent usage of present tense for this throughout the manuscript.**

The frequency of filter sampling was not equally distributed along the whole period. Samples were collected every 3th or 4th day, depending on the sampling period. Therefore, the authors refer to "3 to 4 days"; the expression has been modified accordingly in the revised manuscript.

The past tense used in this sentence makes reference to previous years, when filter samples were collected.

**Reviewer#1. Specific comment 7. P.7 Line 7: Include a reference for the protocol. There are MANY other instances in the paper where the authors make mention of protocols without providing references.**

A reference for the standard gravimetric procedure has been added to the revised paper:

"Alastuey, A., Minguillón, M. C., Pérez, N., Querol, X., Viana, M., and de Leeuw, F.: PM10 measurement methods and correction factors: 2009 status report, ETC/ACM Technical Paper 2011/21, 2011."

**Reviewer#1. Specific comment 8. P.9 Lines 3-6. "It is remarkable that differences in the sampling conditions (RH, size cut) or chemical analysis methods influence the resulting efficiencies obtained for different emplacements. In this study, scattering RH was controlled below 40% preventing the hygroscopic growth of the particles, which could lead to an enhancement in the scattering efficiency." Please clarify why this is remarkable or else delete or rephrase the sentence. The following sentence is also not true and should be modified or removed. Just because RH<40% does not prohibit scattering enhancements, especially for organics. The water uptake is small (on the order of \_10% growth) but not prohibited.**

**Size cut also influences aerosol intensive properties, including single-scattering albedo, Angstrom exponent, etc. This can be seen from any of the papers based on measurements at the NOAA-GMD monitoring sites (Sheridan et al., 2001; Delene and Ogren, 2002; Sherman et al., 2015; Andrews et al., 2011; : : :.).**

Authors agree with the referee. The sentences have been modified accordingly as follows:

"It should be considered that changes in the sampling conditions (i.e. RH or size cut-off) or differences in the chemical analysis methods used on sampled filters can affect the intensive particle optical properties (Delene and Ogren, 2002), and consequently the comparison among the computed MSE and MAE. In fact, the resulting efficiencies can be biased by the cut-off inlet, given

that absorbing aerosols tend to be predominately in the sub-micron fraction (Andrews et al., 2011). In this study both  $\sigma_{sp}$  and  $\sigma_{ap}$  were collected using a PM<sub>10</sub> cut off inlet, thus guaranteeing uniformity among the performed optical measurements. An exception occurs at MSA, where a PM<sub>2.5</sub> cut-off inlet was used until March 2014 and then replaced by a PM<sub>10</sub> inlet. However, an estimation of the influence of the inlet change on the resulting MSE and MAE at MSA is difficult to achieve, given the relatively short  $\sigma_{sp}$  and  $\sigma_{ap}$  time series available thus preventing performing two different MLR analyses for the two fractions. Moreover, scattering RH was controlled below 40% at MSY and MSA in order to minimize the hygroscopic growth of the particles and then prevent a significant enhancement in the scattering efficiencies."

**Reviewer#1. Specific comment 9. P.10 Line 7: Change 'PM10 levels' to "'PM10 mass concentrations'".**

"PM<sub>10</sub> levels" has been rephrased as "PM<sub>10</sub> mass concentrations" in all the instances throughout the revised paper.

**Reviewer#1. Specific comment 10. P.10 Line 10: Change "PM10 load." To "'PM10 mass concentrations". Please do this for all instances in the manuscript.**

The expression "PM10 load" has been rephrased as "PM<sub>10</sub> mass concentrations" in all the instances throughout the revised paper.

**Reviewer#1. Specific comment 11. Fig.3b. PM10 mass concentration at Montseny is nearly as high in March as in June- July and is higher than in August but this is not discussed at all.**

The following paragraph has been added to the revised manuscript aiming to discuss the aforementioned seasonal variability of PM10 mass concentration:

"It is remarkable the PM10 concentration peak observed in February and March at MSY, which might be attributed to the winter regional pollution episodes typical of the WMB (Pandolfi et al., 2014a). Such scenarios are characterized by anticyclonic conditions which favor the accumulation of pollutants close to the emission sources, and the subsequent transport of pollutants towards the station with the daily increase of the PBL. Pandolfi et al. (2014b) and Pey et al. (2010) reported high nitrate concentrations during these atmospheric conditions at MSY, in agreement with the increased contributions of *Secondary nitrate* shown in Fig. 3b during this time of the year period. The relatively low PM<sub>10</sub> concentration observed in August at BCN and MSY could be partially explained by reduced anthropogenic activities in the Barcelona metropolitan and industrial areas as a result of the holiday period in Spain. This result is supported by the minima absolute contributions observed in August for *Industrial* and *Traffic* sources at BCN (0.7 and 2.9  $\mu\text{g m}^{-3}$ , respectively) and for the *Industrial/Traffic* source at MSY (1.2  $\mu\text{g m}^{-3}$ ). The higher precipitation rates observed in August compared to June-July

(Perez et al., 2008) could also significantly contribute to reduce PM<sub>10</sub> concentrations at MSY. Conversely at MSA, the highest PM<sub>10</sub> concentration was observed in August probably due to the frequent Saharan dust events affecting the mountain top site, in accordance with the highest absolute contribution found for the *Mineral* source in August (3.9 µg m<sup>-3</sup>)."

**Reviewer#1. Specific comment 12. Fig(s).4. Please use site abbreviations as either as sub-plot titles or legend labels in fig(s) 4 to make it easier to look at the figures, without needing to go back and forth between plots and caption to see which plot corresponds to which site.**

The corresponding site acronyms have been added to each plot of Fig. 4.  
The correlation plot for the SSA parameter has been removed from Fig. 4

**Reviewer#1. Specific comment 13. P.12 Lines 4-5: The assertion that "Aged organics at MSA (29%) and Ammonium sulfate at MSY (24%) were the dominant sources throughout the year and reached the largest absolute contribution in summer" is not supported by Fig.3. The Mineral source at MSA is comparable to Aged Organics during several months of spring/summer and organics are equal to or exceed ammonium sulfate for several months at MSY. Please reword this assertion to better reflect the data in Fig.3.**

Following the referee's suggestion the paragraph has been modified as follows:

"Differently from BCN, a higher relative contribution of secondary sources, some of them related with natural processes, was observed at MSY and MSA (3b and 3c). Increased contributions of *Secondary sulfate* were observed in summer (29% and 8% at MSY and MSA, respectively), whereas *Secondary nitrate* maximized in winter (17% and 11%). *Aged organics* showed the highest contribution in relative terms in winter (30% and 45% at MSY and MSA, respectively); however the highest absolute contributions were observed in summer (4.8 and 4.1 µg m<sup>-3</sup>). This result is in agreement with the higher SOA formation found at MSA (Ripoll et al., 2015a) and MSY (Minguillón et al., 2015) during the warm period. The *Mineral* source (19% and 27% at MSY and MSA, respectively) maximized in summer, although high contributions were also observed in spring. Similarly to BCN, *Aged marine* (14% and 13% for MSY and MSA, respectively) and *V-Ni bearing* (5% and 11%) sources showed the highest contribution in summer, whereas the *Industrial/Traffic* source maximized in winter (11% and 17%)."

**Reviewer#1. Specific comment 14. P.12 Lines 14-16. This has already been mentioned more than once so the sentence should be deleted.**

The sentence has been removed from the revised paper.

**Reviewer#1. Specific comment 15. P.12 Line 12. Add the word 'Mass' to the beginning of Sect. 3.3 title and to 'absorption efficiencies' and 'scattering efficiencies' throughout this section.**

The text has been modified accordingly to the referee's comment.

**Reviewer#1. Specific comment 16. P.12 Lines 17-24. This passage has already been discussed in previous sections and is not a result. Therefore, it should be deleted.**

The paragraph has been removed from the revised paper.

**Reviewer#1. Specific comment 17. P.13 Line 2: Change the word 'coefficient' to 'MSE'.**

The word "coefficient" has been replaced by "MSE" following the referee's suggestion.

**Reviewer#1. Specific comment 18. P.13 Lines 31-32: "Interestingly, a higher scattering wavelength dependence was observed for those sources with higher contribution from anthropogenic tracers which are mainly present in the fine mode (Table 2)." This is to be expected. Size distributions with higher contributions from the fine mode will possess larger variation of scattering coefficient with wavelength than size distributions with larger contributions from coarse mode aerosol.**

The sentence has been removed from the text.

The results presented for SAE (section 3.3 of the discussion paper) and SSA (section 3.5 of the discussion paper) optical parameters, obtained for specific aerosol sources, have been moved to a new section (Section 3.3.1) included in the revised manuscript.

**Reviewer#1. Specific comment 19. P.14 Line 19: Please clarify what you mean by "European scenarios".**

The paragraph has been modified for a better understanding. Further information on atmospheric European scenarios affecting the MSA mountain-top site can be found in Ripoll et al., 2014 and 2015.

The text in the revised paper is now as follows:

"The large MAE observed for *Secondary nitrate* at MSA ( $0.364 \pm 0.023 \text{ m}^2 \text{ g}^{-1}$ ) was due to the fact that this source explained around 20% of the measured EC concentration (Fig. 2a). Recently, Ripoll et al. (2015b) have shown the increased concentration of nitrate, ammonium, EC and traffic/industrial tracers at MSA under European scenarios. Such scenarios are characterized by the transport of polluted air masses at high altitude from central and Eastern Europe to the MSA site. This fact may

explain the internal mixing of BC particles in the chemical profile of *Secondary nitrate*, and consequently the high MAE values found for this source at MSA."

**Reviewer#1. Specific comment 20. P.15 Lines 9-12:** "Both sources presented inverse seasonal cycles following the seasonal variation of mass contributions, with Ammonium sulfate maximizing in summer at MSY (46%) whereas showing similar contribution throughout the year at MSA. Conversely, Ammonium nitrate mainly governed the light scattering in winter (42% and 29% at MSY and MSA)." Please change the wording of the first sentence, as the phrase 'inverse seasonal cycles' is not clear. Wording similar to this is used in other places to describe the cycles and should be fixed. It is clearer to simply state something along the lines of "The annual cycles of ammonium sulfate and ammonium scattering coefficients follow those of the PM10 mass concentration, with summer maxima and winter minima". The assertion that there are similar ammonium sulfate contributions throughout the year at MSA is not supported by Fig.3h, which indicates that the fraction of light scattering attributed to ammonium sulfate is highest in Aug-Sept and lowest in Nov-Dec.

Following the referee's indications the sentence has been modified as follows:

"The annual cycle of *Secondary sulfate* and *Secondary nitrate* scattering coefficients followed those of the PM<sub>10</sub> mass concentration, with maxima in summer (46% and 35% at MSY and MSA, respectively) and winter (42% and 29%), respectively."

**Reviewer#1. Specific comment 21. P.15 Lines 15-17:** "Light absorption appeared to be almost dominated by the Traffic source at BCN and in a minor proportion by the equivalent Industrial/Traffic at MSY and MSA (Fig. 3d, e, f), showing high contributions in winter (65%, 42%, 22%) despite the relative low mass concentration (23%, 11%, 17%)." This is one of many instances throughout the paper where the wording probably does not convey the authors' intentions. The meaning of 'almost dominated' is unclear. Light absorption coefficient is either dominated by Industrial/Traffic or it is not. Based on Figs.3d-3e, it looks as if it is only dominated by Industrial/Traffic during non-summer months at BCN, although it clearly exerts the major influence (>40%) at MSY. I also do not understand the meaning of "a minor proportion by the equivalent Industrial/Traffic at MSY and MSA". The influence of Industrial/Traffic (>40-50% at MSY and >20% at MSA) is neither dominating or minor. Please clarify this and similar statements throughout the document so that their meaning reflects your intentions. You do a much better job on P.15 Lines 30-31.

Following the referee's suggestion the sentence has been modified as follows:

"The *Traffic* source at BCN and the *Industrial/Traffic* source at MSY clearly exerted the major influence on light absorption contributing 54% and 41% to  $\sigma_{ap}$ , respectively, despite the relative low PM<sub>10</sub> contributions (16% and 10%, respectively). Maxima contributions were observed in winter at

BCN for the *Traffic* source (65%) and in October-January at MSY for the *Industrial/Traffic* source (46%), however a lower influence of *Industrial/Traffic* was observed on average at MSA (18%) (Fig. 3 d, e, f)."

"P.15 lines 30-31" have been removed from the revised paper.

**Reviewer#1. Specific comment 22. P.15 Lines 20-21:** "Therefore, *Traffic*, *Industrial/Traffic* and *V-Ni* sources which highly influence air quality also have caused an important effect on radiative forcing, particularly in those sites closer to the emission sources." This assertion may be true but cannot be supported, given the measurements available in the current study. Only absorption coefficient data is available at BCN (the main site influenced by these sources) and radiative forcing depends primarily on aerosol optical depth (which in turn is largely controlled by scattering coefficient). As such, I recommend that the authors either remove this statement or provide more support for it, given the available data.

The authors agree with the referee, this study does not include any calculation on radiative forcing. The term "radiative forcing" has been removed from the revised paper.

The sentence has been modified as follows:

"Therefore, *Traffic*, *Industrial/Traffic* and *V-Ni bearing* sources, which highly influenced air quality, also significantly contributed to  $\sigma_{ap}$ , and especially in those sites closer to the emission sources."

**Reviewer#1. Specific comment 23. P.15 Line 26-P.16 Line 3:** A summary of results should be placed in the Summary and Conclusions section, not in the Results section.

According to the referee's comment the paragraph has been removed from the paper.

**Reviewer#1. Specific comment 24. P.15 Lines 26-27:** "As a summary, we have shown that the main target pollutant sources affecting air quality degradation have caused important effects on light extinction in the northwestern Mediterranean." This sentence should be clarified. You cannot state anything regarding light extinction at BCN without measurements of light scattering coefficient, which represents the major contribution to light extinction coefficient.

The authors agree with the referee, the sentence has been removed from the paper.

**Reviewer#1. Specific comment 25. P.16 Line 1:** Please remove the phrase "As a novelty,".

The expression "As a novelty" has been removed from the text.

**Reviewer#1. Specific comment 26. P.16 Line 19: What ‘published results’? Please cite reference(s) to support this.**

The sentence has been modified as follows:

“According to published results (Ryan et al., 2005 and references therein)”

**Reviewer#1. Specific comment 27. P.17 Line 4: State at which site you are discussing the SSA. You state that it is MSY in the caption of Fig.4 but it should also be stated in your discussion, so that the reader does not need to go back and forth between the discussion and figure captions.**

According to the referee’s general comment 2 and specific comment 30, the results presented for the simulation and trend analysis of the SSA parameter have been removed from the revised paper.

**Reviewer#1. Specific comment 28. P.17 Line 5: The slope of modeled versus measured SSA is 0.80, which is not close to 1. Please reword this.**

The sentence is not included in the revised manuscript given that the simulation of the SSA parameter has been removed from the text.

**Reviewer#1. Specific comment 29. P.17 Line 15: Since trend study was only done for MSY, the section title should be rephrased to more accurately represent the section contents. This could be as simple as “Long-term trends in scattering and absorption coefficients at MSY”.**

The title of section 3.6 has been rephrased accordingly to the referee’s suggestion.

**Reviewer#1. Specific comment 30. P.17 Lines 19-21: “Despite a larger uncertainty was found for the modeled SSA, this technique allowed to further investigate the temporal trend of this important parameter and its relation with changes in atmospheric composition (Fig. 7).” Marginal agreement of measured and model SSA ( $R^2=0.42$ , slope =0.80) during the 2010-2014 period at MSY (when agreement should be best, since the authors use the same period to both generate and evaluate the model) likely makes it impossible to state much about any long-term trends in SSA at MSY. As such, I believe that the discussion of SSA trends at MSY should be removed from the paper.**

Authors agree with the referee’s comment, the low correlation obtained for the modeled-observed pairs of SSA prevent to accurately estimate any trend for the SSA parameter. Following the referee’s suggestions the SSA trend study at MSY has been removed from the revised manuscript.



**Reviewer#1. Specific comment 31. P. 18 Lines 4:6: "A marked decline was also observed for nitrate and sulfate PM in other European monitoring sites since 1990, as outlined in the EMEP report 1/2016.". Please provide a reference for the EMEP report. Please do the same for other instances where sources are named but not referenced.**

The following reference has been included for the EMEP report:

"as outlined in the EMEP report 1/2016 (Colette et al., 2016)."

"Colette et al., 2016. Air pollution trends in the EMEP region between 1990 and 2012. Joint Report of the EMEP Task Force on Measurements and Modelling (TFMM), Chemical Coordinating Centre (CCC), Meteorological Synthesizing Centre-East (MSC-E), Meteorological Synthesizing Centre-West (MSC-W). Kjeller, NILU (EMEP: TFMM/CCC/MS-C-E/MS-C-W Trend Report) (EMEP/CCC, 01/2016)."

**Reviewer#1. Specific comment 32. P.18 Lines 7-17: Please cite references for all of the claims made in this paragraph, since they are not supported by the data presented in this manuscript. Were the claims from the Pandolfi et al. (2016) paper? If so, you should state this and probably not spend a paragraph summarizing a different study. Simply state (as you did in first sentence of the paragraph) that the causes of reductions in most sources at MSY are discussed in Pandolfi and then move on to how your study contributes to the knowledge. If not, please provide the sources to justify the assertions.**

Authors consider that the causes leading to a reduction in some of the chemical compounds and sources at MSY should be included in the text, in order to better assess the scattering and absorption optical trends and its relation with trends in atmospheric composition.

Assertions regarding decreasing trends for the chemical compounds and sources at MSY are based on the results published by Querol et al., 2014 and Pandolfi et al., 2016. These references have been included throughout the paragraph.

The text in the revised paper is now as follows:

"Querol et al. (2014) and Pandolfi et al. (2016) investigated trends of PM chemical components and aerosol sources at MSY, providing further explanation on the causes leading to the reduction of the atmospheric pollutants in the area. The financial crisis affecting Spain from 2008 contributed to reduce the ambient PM concentrations. A decrease in *Secondary nitrate* can be explained by the reduction of ambient NO<sub>x</sub> and NH<sub>3</sub> concentrations (Querol et al., 2014). The decreasing trend of the *Secondary sulfate* source may be supported by the reduction of sulfate particles, mainly attributed to the gas desulfurization at several facilities (Pandolfi et al., 2016). A decrease in secondary sulfate may be also explained by the 75% reduction of SO<sub>2</sub> concentration in the Barcelona harbor, supported by the regulation of sulfur content in shipping emissions in EU harbors from 2010 (Schembari et al., 2012). This regulation together with the 2007 ban around Barcelona on the use of heavy oils and petroleum coke for power generation, which contributed to a drastic decrease in V

and Ni concentrations (Querol et al., 2014), were the main reasons supporting the observed reduction of the contribution of the *V-Ni bearing* source. "

**Reviewer#1. Specific comment 33. P.18 Lines 22-23: "Interestingly, the SSA showed a significant decreasing trend of -0.11 % y-1 (-0.001 yr-1) leading to a total reduction (TR) of 1.24 % since 2004 at MSY, pointing that the atmosphere is getting significantly darker." A change in SSA of 0.01 is relatively small and does not imply that the atmosphere is getting significantly darker.**

Authors agree with the referee.

The sentence is not included in the revised manuscript given that the SSA trend study has been removed from the paper.

**Reviewer#1. Specific comment 34. P. 18 Lines 25-28: "Differences in the SSA reduction at both sites might be explained by the severe pollution episodes taking place in the Po Valley resulting in a higher dominance of absorption in the light extinction process, compared to MSY which is representative of a less polluted environment." You should provide some reference for this. If not, the decreasing SSA could just as easily be due to larger reductions in scattering than absorption.**

These lines refer to the study published by Putaud et al. (2016). This study showed that the increasing biomass burning emission sources during the colder period contributed to decrease the SSA parameter in the Po Valley. In order to support this result, Putaud et al. (2016) showed that the ratio absorption coefficient/EC concentration increased between 2005 and 2010, especially for the highest values which were observed during the colder months. This result was attributed to the increasing concentrations of other light-absorbing substances, such as brown carbon, during cold months, when wood burning for domestic heating was used more and more in northern Italy.

The reference "Putaud et al. (2016)" has been added in more than one instance throughout the paragraph.

Given that the SSA trend study was removed from the text the paragraph has been rephrased as follows:

"Statistically significant downward trends of PM mass concentration,  $\sigma_{sp}$ ,  $\sigma_{ap}$  and SSA were found in the Po valley (Italy) for the period 2004-2010 (Putaud et al., 2014). A higher decreasing rate was observed for  $\sigma_{sp}$  (-2.8 % yr<sup>-1</sup>) compared to  $\sigma_{ap}$  (-1.1 % yr<sup>-1</sup>), likely due to the increasing contribution of light-absorbing organic matter to light absorption during cold months in the Po Valley (Putaud et al., 2014). In the present study, smaller differences between  $\sigma_{sp}$  and  $\sigma_{ap}$  were observed at MSY, accounting the total reduction trends for -50% and -45%, respectively. This fact might be explained by the different background sites considered; whereas the Po Valley is a highly polluted area, MSY is representative of a cleaner environment where biomass burning emissions, which highly contribute to light absorption, are considerably lower (Minguillón et al., 2015; Ealo et al., 2016)."

**Reviewer#1. Specific comment 35. P.18 Lines 29-34: This is another example of claims being made (and percentages brought up) without any references for these numbers or results. Please include sources/references for these numbers.**

The paragraph has been removed from the text.

Most of section 3.6 has been rephrased and changes are directly included in the revised paper.

**Reviewer#1. Specific comment 36. P.19 Lines 12-13: “The reduction in the SSA trend points out the increasing prominence of absorption in the light extinction process in the NW Mediterranean.” This represents another claim that is unsupported by the data. An apparent 1% decrease in SSA at a single site does NOT point to increasing prominence of absorption in the light extinction process in the NW Mediterranean region. Please either provide more support for this assertion or delete it.**

Given that the SSA trend study was removed from the paper, section 3.6 has been substantially modified. Changes are directly shown in the revised paper.

**Reviewer#1. Specific comment 37. P. 19 Lines 16-23: This discussion of radiative forcing and relation to policy lies well beyond what can be stated, based on data/results from this manuscript. Please either change the wording so that it is supported by your results or else remove.**

Authors agree with the referee. The term “radiative forcing” and the conclusions based on this approach have been removed from the paper. Given that SSA trend analysis was removed from the text, section 3.6 and conclusions of the revised manuscript have been substantially modified. Changes are directly shown in the revised paper.

**Reviewer#1. Specific comment 38. P. 20 Lines 31-32: “A total reduction (TR) of -1.12% in the SSA was mainly motivated by the heterogeneous and non-selective reduction of key aerosol sources showing opposite effects on radiative forcing.” The assertion regarding effects on radiative forcing is not supported by the data and should be removed.**

We agree with the referee, the sentence has been removed from the text. Following previous referee’s suggestions the term radiative forcing has been removed from the paper.

**Reviewer#1. Specific comment 39. P.20 Line 34-Page 21 Line 8: “However, these measures have resulted in a more pronounced reduction of light-scattering aerosol sources (Ammonium nitrate, Ammonium sulfate), leading to an increase of the incoming solar radiation and therefore**

contributing to climate warming. This positive radiative effect is enhanced by the less effectiveness of air quality strategies for reducing light-absorbing sources containing dark particles. A decrease in the SSA trend points to a darkening of the atmosphere and consequently to a progressive predominance of absorption in the light extinction process in the NW Mediterranean. Accordingly to the results presented in this work, future strategies need to focus on preferentially reducing atmospheric aerosols mainly originated from combustion sources. Industrial/Traffic and V-Ni aerosol sources, which highly contributed to air quality degradation but also to light absorption, should be abated thus addressing win-win policies aimed to improve air quality and mitigate climate warming

in the NW Mediterranean.”

Where is the evidence for increasing in solar radiative and contributions to climate warming? This and the policy recommendations are completely unsubstantiated by the data and either need to be justified or removed. A small and questionable decrease in SSA (based on poor correlation and marginal agreement between modeled and measured SSA during common period) at a single site cannot be used to make claims regarding darkening of the atmosphere. See my many comments above regarding assertions that are unsupported.

Authors agree with the referee, we do not provide any results on radiative forcing, nor solar radiation measurements, for this reason the term “radiative forcing” and the conclusions making reference to this term have been removed from the paper.

Moreover, as outlined in previous comments, the SSA trend analysis has been removed from the manuscript and therefore section 3.6 and section 4 have been substantially modified in the revised paper. In the following lines it is shown the last paragraph from section 3.6 of the revised paper, as a representation of the modifications carried out in this section. Additional changes introduced in the manuscript are directly shown in the revised paper.

“Further research on light scattering and absorption long-term trends and its relation with changes in atmospheric composition is needed to better understand the role of aerosols on optical properties and on the climate system. Based on the published studies and the present results, further efforts focusing on the reduction of atmospheric pollutants containing BC particles (mainly emitted from fossil fuel combustion and biomass burning sources) need to be addressed. Given the toxicity of their chemical tracers, as well as their large contribution to light absorption, *Industrial/Traffic* and *V-Ni bearing* sources must be reduced through the implementation of win-win policies, aiming to improve air quality and public health, and mitigate climate warming.”

#### **Anonymous Referee# 2.**

**This study showed not only aerosol source contributions based on a positive matrix factorization (PMF) analysis, but also mass scattering and absorption efficiencies (MSE and MAE) of different**

aerosol sources by using multilinear regression method at urban, regional and remote backgrounds in the Spain. Although the results and discussion were documented well, there are several important shortcomings.

**Reviewer#2. Specific comment 1.** While the detailed pedagogical description of the approach is appreciated, the paper overall must be shortened. There are many repetitions in the text or not essentially needed with many references. This review strongly suggest that text must be made more succinct. For example, in INTRODUCTION, the authors explained overall aspects of aerosols in climate-air quality research. Most of them are overstated and not directly related with the results of this study. The words “From air quality to climate” in title also should be removed. Summary and conclusions also should be shortened; highlight the major findings succinctly and provide directions/implications of this work.

Following recommendations from both referees, some sections of the manuscript including abstract, introduction and conclusions have been rephrased in the revised manuscript. Those parts of the text which were repeatedly commented have also been removed or rephrased. Overall, substantial changes have been introduced in the revised paper aiming to improve readability of the text and better reflect the achieved results.

The title has been modified accordingly to the referee’s comment.

**Reviewer#2. Specific comment 2.** Generally, source apportionment by PMF model shows the contributions of aerosol chemical properties from various sources, such as traffic (vehicle), biomass burning, dust (road dust), marine, industry, secondary nitrate, secondary sulfate, ship, etc. However, the sources given in this study are aerosol compositions, except for industrial/Traffic and Marine. Firstly, the authors should show the chemical compositions and discuss the characteristics during the study period. The explanation of major emissions sources of the aerosols also provided. Secondly, more detailed descriptions for source profiles should be given. For example, V-Ni at MSY originated mainly from shipping emissions (see section 3.3), why EC is not considered at the source profile.

According to the Referee’s suggestion, the name of *Ammonium nitrate* and *Ammonium sulfate* aerosol sources have been replaced by *Secondary nitrate* and *Secondary sulfate*, respectively.

The aerosol sources and contributions discussed in the present paper for BCN and MSY were firstly published by Pandolfi et al. (2016) for the same study period. Therefore, further information on the results of PM10 and PM2.5 chemical compounds and PMF source contributions at BCN and MSY can be found in Pandolfi et al. (2016). Authors consider that an extended discussion on the PMF results at BCN and MSY would provide repetitive information.

The novelty of the present paper, regarding PMF analysis, are the results presented for the source chemical profiles and contributions at MSA, and that's the reason why results from PMF at MSA are extensively discussed in the paper compared to the results presented for MSY and BCN, which were firstly and widely discussed in Pandolfi et al., 2016.

However, the resulting PM source contributions are just a tool to obtain the main goal of the present paper which is focused on providing, for the first time, mass scattering and absorption efficiencies (MSE and MAE) for specific aerosol sources. Additionally, the paper aims to assess the PMF-MLR technique to accurately simulate scattering and absorption coefficients when chemical speciation data is available.

A discussion on the PM chemical compounds at MSA is not provided given that doing so detracts the focus of the paper. Previous studies deployed at MSA have presented the PM<sub>10</sub> and PM<sub>1</sub> chemical composition at this site (Ripoll et al., 2015).

Authors agree with the referee, further information on the source chemical profiles at BCN and MSY should be provided in the paper. The source chemical profiles for BCN and MSY have been added to the revised supporting material. Even though this information was previously reported in Pandolfi et al. (2016), it is needed to better understand the changing chemical profile of the common aerosol sources at the three different sites.

The following Figure S2 has been added to the revised supporting material.

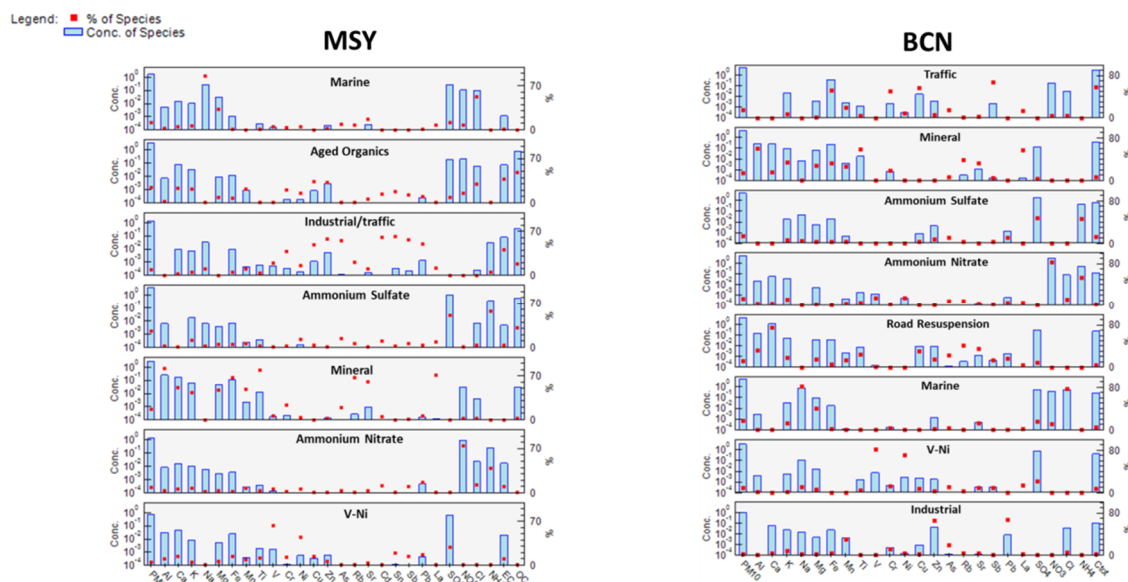


Figure S2. Source chemical profiles obtained by means of the PMF model at BCN and MSY for the period 2004-2014 (Pandolfi et al., 2016).

We guess that the referee is making reference to MSA in the last sentence, given that the unique chemical profile resulting from applying a PMF model shown in the discussion paper makes reference to the results presented for MSA.

It should be noted that the PMF model was run automatically and then we cannot choose the apportionment of specific species to the different sources, so that the *V-Ni bearing* source at MSA, constituted by specific chemical species, is an automatic output from the PMF model. Differently from BCN and MSY, the resulting *V-Ni bearing* source at MSA does not include EC in the chemical profile given that EC is mainly attributed to the *Aged organics* and *Ammonium nitrate* sources at this site. This fact might be related to the high altitude and far position of MSA from the Mediterranean coast and shipping emissions. Whereas MSY is affected by the direct shipping emissions from the Mediterranean coast, the MSA site might be influenced by atmospheric long range transport, and therefore the *V-Ni bearing* source at both sites might be internally mixed with different chemical species.

The following sentence has been added to the revised manuscript:

"Differently from BCN and MSY, the *V-Ni bearing* source at MSA was not enriched in EC possibly because of the high altitude of this station and its position, far from the western Mediterranean coastline and shipping emissions."

**Reviewer#2. Specific comment 3. It is not fully explained how the authors determined the scattering and extinction efficiencies (MSE and MEE) of chemical species by using the Multilinear regression method. Eqs. 1 and 2 are not enough. This reviewer strongly suggests that detailed steps for getting the MSE and MEE of chemical species by using the multilinear regression have to be present in main text or in the supplement.**

The MLR analysis for estimating MSE and MAE of aerosol particle sources is based on the IMPROVE algorithm (Hand and Malm, 2007 and references therein). Equations 1 and 2 presented in section 2.3 of the discussion paper are similar to those equations showed in previous published studies. Authors do not exactly understand which changes should be introduced in the MLR equation.

Section 2.3 (named section 2.4 in the revised paper) has been rephrased for a better understanding. Changes have been directly modified in the revised paper.

**Reviewer#2. Specific comment 4. Regarding to the reconstruction (section 3.5), what is the root-mean-square difference for data given in Figure 4? This reviewer suggests to use percentage difference of bias rather than fractional bias.**

Following the referee's comment, the root-mean-square error (RMSE) has been accordingly calculated for the modeled and measured optical parameters. The RMSE is widely used in modeling evaluation and provides valuable information on the accuracy of the predicted coefficients compared to the observational data.

The following paragraph has been added to the revised manuscript:

"The root mean square error (RMSE) was calculated for the observed-modeled datasets, showing low dispersion and high accuracy in the modeled values. Scattering and absorption coefficients were well reproduced by the model, showing RMSE values of 8.76 and 6.06  $\text{Mm}^{-1}$  for  $\sigma_{\text{sp}}$  at MSY and MSA, and values of 2.61, 0.55 and 0.23  $\text{Mm}^{-1}$  for  $\sigma_{\text{ap}}$  at BCN, MSY and MSA, respectively."

The Fractional bias (FB) is presented in this study, given that published studies applying a MLR model for MSE calculation have also used the FB parameter to assess the accuracy of the model to simulate  $\sigma_{\text{sp}}$  coefficients (Ryan et al., 2005). Therefore, FB has also been used in this study to compare our results with the published studies. The replacement of fractional bias by the percentage of FB does not provide further information on the discussion of the accuracy of the modelled  $\sigma_{\text{sp}}$  coefficients. Authors prefer to keep the FB parameter in the revised paper.

**Reviewer#2. Specific comment 5. Long-term trends in Section 3.6: There is no detailed explanation on Figure 6. There is a critical issue that how we can trust these reconstructed values given in Figure 6 and associated trend analysis results. For example, Collaud Coen et al (<http://www.atmos-chem-phys.net/13/869/2013/acp-13-869-2013.pdf>) reported that, in the Europe, significant trends were not observed for aerosol optical properties at most sites (see Table 8 in the paper). However, this study, this study reports about a scattering TR (total reduction) of -52% since 2004 and -44% in the absorption coefficient. Therefore, the authors should investigated all published literature, especially in Europe, and give a reasonable and reliable explanation with evidences. If there are such distinct decreases in aerosol scattering and absorption properties, is this trend also consistently seen from aerosol optical depth measurements from AERONET/SKYNET and satellite sensors? Also, do PM2.5 concentrations show a decreasing trend over the study period?**

A very good agreement has been found between measured and modeled pairs of scattering ( $R^2=0.88$ ) and absorption ( $R^2=0.8$ ) with slopes close to one at MSY for the period 2010-2014 (Fig. 4 of the paper). In addition, following the suggestion of referee#1 in general comment 1, an independent subset of the period (year 2015) not considered in the MLR analysis has been used in order to further evaluate the accuracy of the modeled scattering and absorption (see general comment 1). Good agreement was found between modeled and measured  $\sigma_{\text{sp}}$  ( $R^2=0.85$ ) and  $\sigma_{\text{ap}}$  ( $R^2=0.76$ ) coefficients, at 525 and 637 nm respectively, showing slopes close to one for the year 2015 at MSY (Fig. 6 of the revised paper). Authors consider that these results support the accuracy of the modeled  $\sigma_{\text{sp}}$  and  $\sigma_{\text{ap}}$  time series in order to carry out the trends study.

Pandolfi et al. (2016) observed significant decreasing trends in PM10 and PM2.5 chemical species concentration and PMF sources contribution for the period 2004-2014 at the BCN and MSY sites. The reference of Pandolfi et al. (2016) is cited throughout the paper, given that PMF source contributions



at BCN and MSY are also used in this study, as is detailed in the discussion paper. Therefore, these results showing decreasing trends on PM<sub>10</sub> and M<sub>2.5</sub> concentrations and their chemical tracers support the observed reduction on the optical properties trends at both sites.

Other studies have been published in the last years showing clearly that the concentrations of PM and other air pollutants such as sulfur dioxide (SO<sub>2</sub>) and carbon monoxide (CO), have markedly decreased during the last 15 years in many European countries (EEA, 2013; Barmpadimos et al., 2012; Cusack et al., 2012; Querol et al., 2014; Guerreiro et al., 2014 among others). Cusack et al. (2012) reported the reduction in PM<sub>2.5</sub> concentrations observed at regional background (RB) stations in Spain and across Europe. Barmpadimos et al. (2012) have also shown that PM<sub>10</sub> concentrations decreased at some urban and rural background stations in five European countries. Henschel et al. (2013) reported the decrease in SO<sub>2</sub> levels in six European cities. EEA (2013) also reported general decreases in NO<sub>2</sub> concentrations.

A less number of studies focused on optical properties trends analysis were published in Europe. For example, Putaud et al. (2014) found downward trends for PM, scattering, absorption and SSA series for the period 2004-2010 in the northeast of Italy.

Few studies clearly support the reduction of the atmospheric PM in many European measurement sites, which consequently leads to a decrease in the scattering and/or absorption trends.

Aerosol optical properties measurements are relatively recent in Europe compared to the EEUU, as shown in Collaud Cohen et al., 2010. The latter study presents a global overview on trends study of optical parameters, however no significant decreasing trends were observed in the European sites. This fact may be due to differences in the time period for major European reductions relative to the time period covered by the aerosol optical property measurements. The limited number of available datasets as well as the characteristics of the sites, which might not be representative for trends study (e.g. high altitude or marine), also supposed a limiting factor for trends study (Collaud Cohen et al., 2010).

Columnar measurements are affected by atmospheric processes and emission sources at regional and continental scales, involving transboundary transport. However, surface data is mainly affected by local and regional emission sources which are directly influenced by the air quality regulation strategies. Authors consider that aerosol optical depth measurements should not be included in the revised paper given that the paper focuses on surface measurements, and the decreasing rates of columnar optical parameters cannot be explained by the process occurring at the surface. The trends study of surface scattering and absorption series aims to relate the trends of specific aerosol sources with trends in optical parameters, in order to assess the effects that air quality strategies adopted in recent years are having on light extinction. Therefore, authors think that a trend study of columnar measurements does not fit in the present paper; however it is a good suggestion that will be considered for future studies.

# ~~From air quality to climate;~~ Impact of aerosol sources on optical properties at urban, regional and continental remote levels in the north-western Mediterranean

Marina Ealo<sup>1,2</sup>, Andrés Alastuey<sup>1</sup>, Noemí Pérez<sup>1</sup>, Anna Ripoll<sup>1</sup>, Xavier Querol<sup>1</sup>, Marco Pandolfi<sup>1</sup>.

5 [1]{Institute of Environmental Assessment and Water Research (IDAEA-CSIC), Barcelona, Spain }.

[2]{Group of Meteorology, Department of Applied Physics, Faculty of Physics, University of Barcelona, Spain }.

Correspondence to: Marina Ealo (marina.ealo@idaea.csic.es)

## Abstract

10 ~~Linking the effects of airborne particulate matter (PM) on air quality and climate is a challenge that requires integrating the chemical and optical properties of atmospheric aerosols.~~ Further research is needed to reduce the existing uncertainties on the effect that specific aerosol sources have on ~~radiative forcing~~ light extinction and consequently on climate, ~~thus supporting the assessment of future mitigation strategies, which should be focused on both air quality and climate, and not acting separately.~~ This study presents a new approach aimed ing at quantifying the mass scattering and absorption  
15 efficiencies (MSE and MAE) of different aerosol sources at urban (Barcelona-BCN), regional (Montseny-MSY) and remote (Montsec-MSA) background sites in the northwestern (NW) Mediterranean. An analysis of source apportionment to the measured multi-wavelength aerosol ~~the measured light~~ scattering ( $\sigma_{sp}$ ) and absorption ( $\sigma_{ap}$ ) coefficients was performed by means of a multilinear regression (MLR) model for the periods 2009-2014, 2010-2014 and 2011-2014 at BCN, MSY and MSA. The source contributions to PM<sub>10</sub> mass concentration, identified ~~at the three sites~~ by means of the Positive Matrix  
20 Factorization (PMF) model, were used as dependent variables in the MLR model. With this approach we addressed both, the effect that aerosol particle sources have on air quality and their potential effect on light extinction through the determination of their MSE and MAE. An advantage of the presented approach is that the calculated MSE and MAE take into account the internal mixing of atmospheric particles. ~~PMF source contributions were obtained following the same procedure and using unique large datasets of PM chemical speciated data collected during 2004-2014 at BCN and MSY and during 2010-2014 at MSA.~~ This new approach presents the advantage of taking into account the internal mixing state of atmospheric aerosols for  
25 scattering and absorption source apportioning.

Seven aerosol sources were ~~obtained~~ identified at MSA and MSY, and eight sources at BCN. *Mineral, Aged marine, AmmoniumSecondary sulfate, AmmoniumSecondary nitrate* and *V-Ni bearing* sources were common at the three sites. ~~Specific pollutant sources related to the direct exposure to anthropogenic emissions were isolated at BCN (Traffic, Industrial/metallurgy and Road-resuspension~~ were isolated at BCN, whereas ). ~~As a consequence of the atmospheric transport, the main tracers of these anthropogenic sources were found internally mixed with local pollutants at the~~

30

~~background sites (Industrial/Traffic and). Aged organics source, with a marked biogenic contribution, was/were solely identified at MSY and MSA background sites.~~

The highest ~~scattering efficiencies~~MSE were ~~found-observed~~ for ~~Ammonium~~Secondary sulfate ( $4.5$  and  $10.7 \text{ m}^2 \text{ g}^{-1}$  ~~at MSY and MSA, respectively~~), ~~Ammonium~~Secondary nitrate ( $8.8$  and  $7.8 \text{ m}^2 \text{ g}^{-1}$ ) ~~at MSY and MSA respectively~~. These sources dominated ~~dominating~~ the scattering throughout the year with marked seasonal trends. ~~The V-Ni bearing source, originating mainly from shipping in the area under study, originated mainly from shipping emissions,~~ simultaneously contributed to both  $\sigma_{\text{sp}}$  ~~scattering~~ and  $\sigma_{\text{ap}}$  ~~absorption~~, being the second most efficient ~~light-absorbing~~ ~~absorptive~~ source in BCN ( $\text{MAE}=0.9 \text{ m}^2 \text{ g}^{-1}$ ) ~~, with notable effect also at MSY and MSA ( $0.5$  and  $0.2 \text{ m}^2 \text{ g}^{-1}$ ). However, the~~ Traffic source at BCN and the ~~equivalent~~ Industrial/Traffic at MSY ~~and MSA exhibited the highest MAE ( $1.7$  and  $0.9 \text{ m}^2 \text{ g}^{-1}$ , respectively). These sources were the major contributors to the measured  $\sigma_{\text{ap}}$  at BCN and MSY, however At MSA, Secondary nitrate exerted the highest influence on  $\sigma_{\text{a}}$  ( $\text{MAE}=0.4 \text{ m}^2 \text{ g}^{-1}$ ).~~

Sources predominantly composed ~~by-of~~ fine and relatively dark particles ~~highly contributing to light absorption~~, such as Industrial/Traffic, Aged organics, and V-Ni, were simultaneously characterized ~~by-with-a~~ low single scattering albedo (SSA) and high scattering ~~Ångström~~Angstrom exponent (SAE). Conversely, Mineral and Aged marine showed the ~~lowest-highest~~ SAE and the ~~lowest-highest~~ SSA, being scattering the dominant process in the light extinction.

The good ~~agreement found correlation and the low bias observed~~ between modeled and measured  ~~$\sigma_{\text{sp}}$  and  $\sigma_{\text{ap}}$~~  particle optical properties allowed ~~for~~ the reconstruction of ~~scattering, absorption and SSA- $\sigma_{\text{sp}}$  and  $\sigma_{\text{ap}}$  long-term-time~~ series ~~duringover~~ the period 2004-2014 at MSY ~~by means of the PMF-MLR technique~~. Significant decreasing trends were found ~~at MSY~~ for the modeled  $\sigma_{\text{sp}}$  ~~scattering~~ and  $\sigma_{\text{ap}}$  ~~absorption~~ ( $-4.6$  and  $-4.1 \text{ \% y}^{-1}$ ) ~~coefficients. Interestingly, the observed reduction in the SSA ( $-0.11 \text{ \% y}^{-1}$ ) might suggests a less effectiveness of the air quality strategies focused on reducing pollutants containing black carbon (BC) particles, which highly contribute to light absorption and thus climate warming.~~

## 1. Introduction

Further research on the sources of atmospheric pollutants and their potential effect on climate forcing is needed in order to assess future mitigation strategies. The air quality abatement strategies adopted in the recent years have resulted in a decrease of anthropogenic pollutants in Europe (EEA, 2013; Barmapadimos et al., 2012; Querol et al., 2014; Pandolfi et al., 2016). However, the control of pollutant emissions is currently conflicting involving a trade-off between the impacts on environmental health and the Earth's climate, and therefore current mitigation strategies could increase climate warming while improving air quality (Shindell et al., 2012). Thus, precise measurements of aerosol properties are required to further deepening in the relationship existing between aerosol optical and chemical properties, in order to better understand the link air quality climate and to reduce the current uncertainties on the effects that aerosols have on radiative forcing (IPCC 2007, 2013).

Atmospheric aerosols affect the Earth's climate through the direct scattering and absorption of solar radiation but also through indirect processes acting as cloud condensation nuclei (IPCC, 2007). Precise measurements of aerosol properties are required to reduce the current uncertainties on radiative forcing (IPCC 2007, 2013), and further research aiming at studying the relationship existing between aerosol optical and chemical properties is needed to better understand the link air quality-climate. However, a thorough quantification of the direct and indirect aerosol effects on the Earth's radiative budget is difficult to achieve (Zieger et al., 2012). The high spatial and temporal variability of atmospheric particles along with the large differences in aerosol composition and size (Zieger et al., 2012; Haywood et al., 1999; Andrews et al., 2011; Bond et al., 2013), results in a changing radiative forcing from local to global scales (Collaud Coen et al., 2013). On the global scale, atmospheric aerosols are estimated to cool the Earth system (Chen et al., 2011; IPCC, 2013).

Most aerosol components (mainly sulfate, nitrate, organics and mineral matter) scatter the sunlight causing a net cooling at the top of the atmosphere (TOA); conversely other particles, such as black carbon (BC), absorb solar radiation in the whole visible spectrum, thus warming the atmosphere and causing leading to a net warming at TOA (Jacobson, 2001a; Ramanathan and Carmichael, 2008). On the global scale, aerosols are estimated to cool the Earth system (Chen et al., 2011; IPCC, 2013).

Assessing the role of aerosols on climate forcing often requires reducing their physicochemical properties to a set of parameters that describe their optical properties (Hand and Malm, 2007), such as the mass scattering and absorption efficiencies (MSE and MAE, respectively) (Hand and Malm, 2007). These are key intensive optical parameters that relate the mass concentration of specific chemical species to the particle light scattering ( $\sigma_{sp}$ ) and absorption ( $\sigma_{ap}$ ) coefficients. the aerosol scattering and absorption coefficients with mass concentration of specific species, thus linking the aerosol chemical and optical properties of climate relevant species. MSE and MAE are These intensive optical parameters depending on intrinsic aerosol properties, such as particle effective radius, particle mass density or refractive index, and they are very useful to better parameterize the aerosols direct radiative effect in atmospheric climate models (Seinfeld and Pandis, 1998; Hand and Malm, 2007); and therefore to quantify the potential of aerosols for cooling or warming the Earth-atmosphere system.

However, a thorough quantification of the direct and indirect aerosol effects on the Earth's radiative budget is difficult to achieve, due to the high spatial and temporal variability along with the large differences in aerosol composition and size (Zieger et al., 2012). Aerosols originate from a huge variety of sources (both natural and anthropogenic) and formation and transformation processes, leading to a widely variation in type, composition and mixing state (i.e. Haywood et al., 1999; Andrews et al., 2011; Bond et al., 2013). Moreover, given their short lifetime (from days to weeks) and the number of sources and sinks, the broad spatial and temporal variability of aerosol properties is extremely high and this results in a radiative forcing from local to global scales (Collaud Coen et al., 2013).

The determination of MSE and MAE for specific aerosol components has been subject of research in the last few years. Several studies have been published on focused on determining the MAE-absorption efficiency of black carbon (BC) particles, calculated as the ratio between  $\sigma_{ap}$  aerosol absorption coefficient and elemental carbon (EC) concentrations, obtained by means of thermo-optical analysis on filter samples. Given that BC is the most important light absorbing particle in the atmosphere, its MAE has been extensively studied in literature (i.e. Bond et al., 2013; Reche et al., 2011; Pandolfi et al., 2011, 2014a, among others). In some cases, the MAE of BC has been observed to change depending on the degree of the internal mixing of BC with non-absorbing material, such as sulfate and organic compounds (Jacobson, 2001b; Moffet and Prather, 2009; Ramana et al., 2010; Zanatta et al., 2016). Recently, the potential for organic carbon as an absorber of UV and visible light through their "brown carbon" (BrC) content, has been also reported in literature (e.g. Lu et al., 2015; Updyke et al., 2012). The MSE of different chemical aerosol components has been also broadly extensively reported for many locations (Vrekoussis et al., 2005; Titos et al., 2012; Cheng et al., 2015 and references therein). An example is the study performed by the IMPROVE (Interagency Monitoring of Protected Visual Environments) program, which has been taken-considered as a reference for reporting mass extinction efficiencies (MEE) depending on particle composition (Hand and Malm, 2006 and 2007). Global MSE were-reported for dry ammonium sulfate  $[(NH_4)_2SO_4]$ , ammonium nitrate  $[NH_4NO_3]$ , organic matter (OM), soil dust and sea salt were obtained by means of a multilinear regression (MLR) model. In the IMPROVE model,  $\sigma_{sp}$  long term measurements (from 1990 to 2007) were used as independent variable whereas the aforementioned externally mixed chemical species were used as dependent variables. In addition, the IMPROVE study demonstrated that the reconstruction of  $\sigma_{sp}$  the extinction coefficient can be inversely computed by means of the calculated MSE and the mass concentration of chemical species. Revised algorithms of the IMPROVE equation have been published in literature aiming at reducing the bias on the predicted values, accounting for a 25% overestimate in the  $\sigma_{sp}$  scattering coefficient (Ryan et al., 2005; Pitchford et al., 2007). Opportune correction factors for some chemical species are included in the IMPROVE formula in order to account for the effect of relative humidity in the scattering enhancement. Once the MEE from the IMPROVE algorithm are obtained, the aerosol extinction coefficient can be reconstructed using the concentration of the main chemical components of particulate matter (PM) and the corresponding MEE. However, none of the published studies dealing with the estimation of MSE have considered the internal mixing state of atmospheric aerosols, given that each chemical specie was treated separately from the other. This fact might probably lead to biases in the predicted  $\sigma_{sp}$  due to aerosols not considered in the MLR model. The values of MSE and MAE reported in literature vary

largely from one study to another, and this variability is probably partially due to differences in sampling procedure and data analyses. Nevertheless, the observed variability may also be due to the different mixing state of atmospheric aerosols at different environments.

A broad variability for MSE and MAE coefficients has been found in the literature. Differences arise from the different sampling and analysis methods used for determining chemical and optical properties, but also because the mixing state of atmospheric aerosols which broadly vary from one site to another. Therefore, coefficients obtained in the IMPROVE equation might not be used in other emplacements since MSE and MAE are site dependent and unique coefficients. Revised algorithms of the IMPROVE equation have been published in literature aimed at reducing the bias on the predicted values, accounting for a 25% overestimate in the scattering coefficient (Ryan et al., 2005; Pitchford et al., 2007). For example Ryan et al. (2005) reconstructed light extinction using a concentration power law model, that assumes concentration varying mass scattering efficiencies, resulting in a 2% overestimation for the measured scattering coefficients. This method allows obtaining accurate predicted values for the reconstruction of long term series of optical properties; however, it cannot be used for a reliable calculation of MSE and MAE. Additionally, the internal mixing state of atmospheric aerosols is not considered in none of these methods given that each major chemical specie is treated separately from the other, and probably leading to biases due to aerosols not considered in these studies.

In the present study a different approach of the MLR method ~~was~~ is presented investigated, where the aerosol source contributions obtained by means of the PMF (Positive Matrix Factorization) model, instead of the single chemical species, were used as dependent variables in the MLR model. using PM source contributions obtained by means of the PMF (Positive Matrix Factorization) model as a substitute for chemical species. An important characteristic of the PMF ~~sources~~ factors is that these take into account the internal mixing of atmospheric ~~particles~~ aerosols. In fact, as evidenced by the PMF sources chemical profiles, these are constituted by some main tracers as evidenced by their chemical profiles, which are constituted by the main tracers (which define the source) defining the source but are also enriched in other chemical compounds. With this aim, a source apportionment to PM<sub>10</sub> was performed at Montsec (MSA) by means of the PMF model during the period 2010-2014. PM source contributions obtained at the Barcelona (BCN) and Montseny (MSY) sites using a unique chemical data set of 11 years (2004-2014) were also considered in this study (Pandolfi et al., 2016). From one side ~~r~~ Receptor models such as PMF are powerful and widely used techniques to design air quality strategies (i.e. Viana et al., 2008; Belis et al., 2013), ~~thanks due~~ to the capability of these models to identify key pollutant emission sources and calculate their contributions to the measured PM mass concentration. Actually, Belis et al. (2014) proposed the use of harmonized methods for source apportioning across Europe given the relevant information these models provide for the development and assessment of pollution source abatement measures. On the other side ~~Thus~~, the regression model (MLR) model applied using the PMF of source contributions and the measured to scattering and absorption  $\sigma_{sp}$  and  $\sigma_{ap}$  coefficients allows to quantify quantifying the potential of different aerosol these particle sources ~~for scattering or absorbing~~ to scatter or absorb the visible light, and therefore directly linking the air quality and climate effects of airborne PM.

The PMF+MLR technique was performed for the aerosol scattering and absorption coefficients measured at three sampling sites aiming to calculate the MSE and MAE of the different particle sources identified at urban, regional and remote environments in the NE of Spain since 2010. Furthermore, the computed source contributions obtained from the PMF model and the corresponding MSE and MAE computed by means of the MLR (when optical measurements were available) were used for the reconstruction of the aerosol particle  $\sigma_{sp}$  and  $\sigma_{ap}$  scattering and absorption coefficients over an 11-year period at the MSY regional site, thus allowing trend analyses. This methodology allowed to study long term trends of optical parameters at MSY. Trend analyses of particle optical properties which are extremely relevant for the detection of changes in atmospheric composition depending on changes in natural or anthropogenic emissions, atmospheric processes and sinks (Collaud Coen et al., 2013). A relevant outcome of this new approach is the chance to study the effects that air quality mitigation strategies are having on climate in the area under study. Several studies have shown that the air quality abatement strategies adopted in the recent years have resulted in a decrease of anthropogenic pollutants in Europe (EEA, 2013; Barmadimos et al., 2012; Querol et al., 2014; Pandolfi et al., 2016). However, the control of pollutant emissions is currently conflicting involving a trade-off between the impacts on environmental health and the Earth's climate, and therefore current mitigation strategies could increase climate warming while improving air quality (Shindell et al., 2012). A relevant outcome of this new approach is the chance to study the effects that air quality mitigation strategies are having on climate light extinction in the area under study.

## 2. Methodology

### 2.1 Sampling sites and meteorology

The Western Mediterranean Basin (WMB) is characterized by warm summers and temperate winters with irregular precipitation rates throughout the year. In winter the location of the Azores high-pressure system favours the entry of Atlantic advections that clears the atmosphere out of pollutants. In summer, atmospheric dynamics coupled to local orography result in local/regional circulations with the consequent accumulation of pollutants (Millán et al., 1997). Recirculation and aging of pollutants is favoured by weak gradient atmospheric conditions, scarce precipitation and continuous exposure to solar radiation driving photochemical reactions (Rodríguez et al., 2002; Pérez et al., 2004). Additionally, large mineral dust contributions from Saharan dust events may cause exceedances of the air quality standards (Escudero et al., 2007; Querol et al., 2009). The conjunction of all these processes surrounding the WMB, lead to a radiative forcing among the highest in the world (Jacobson, 2001).

PM chemical and optical measurements were performed at three sampling sites located in the NE Spain (Fig. 1).

The large coastal Barcelona urban area (BCN; 41°23'N, 02°6'E, 80 m a.s.l.) is one of the most populated areas in the Northwestern Mediterranean, resulting in a very high road traffic density. Additionally, the metropolitan area is surrounded by a broad industrial sector area and has one of the main major harbors in the Mediterranean Basin, with a large

number of cruise ships (Pey et al., 2013). ~~The conjunction of these emission sources. All these anthropogenic emission sources highly contribute to the air quality degradation contribute to the largest atmospheric pollution in the area causing important consequences on air quality~~ (Querol et al., 2001; Pey et al., 2008; Pérez et al., 2008; Amato et al., 2009; Reche et al., 2011; Dall'Osto et al., 2013).

- 5 The Montseny regional background station (MSY; 41°19'N, 02°21'E, 720 m a.s.l.) is located in the Montseny natural park in a densely forested area, 50km to the N-NE of the Barcelona urban area and 25km from the Mediterranean coast. Despite the site is far enough from the industrialized and populated Barcelona metropolitan region, it can be affected by anthropogenic emissions transported to inland areas (Pérez et al., 2008).

The Montsec continental background site is a remote high altitude emplacement (MSA; 42°3'N, 0°44'E, 1570 m a.s.l.) placed in the southern side of the Pre-Pyrenees at the Montsec d'Ares mountain range, located 140 km to the NW of Barcelona and 140 km to the WNW of MSY. Despite the high-altitude location and the frequent free troposphere conditions during the cold season, the station can be slightly influenced by anthropogenic emissions during the warmer period, when it is positioned within the planetary boundary layer (PBL), (Ripoll et al., 2014).

10 The three sites are ~~members involved of~~ the Catalanian air quality monitoring network. Additionally, ~~the MSY and MSA stations form are~~ part of the ACTRIS (Aerosol, Clouds and Trace gases Research InfraStructure) and GAW (Global Atmosphere Watch) networks. Aerosol optical properties at the sites are measured following standard network protocols (WMO/GAW, 2016). ~~and then aerosol optical measurements were performed following the standards required by these networks.~~ Further information characterizing physical, chemical and optical properties of atmospheric aerosols detailing the prevailing atmospheric dynamics at the three stations can be found in: Querol et al., (2001); Pey et al. (2009 and 2010);  
20 Reche et al. (2011); Pandolfi et al. (2011 and 2014a); Cusack et al. (2012); ~~Ripoll et al. (2015)~~ and Ealo et al. (2016).

## 2.2 Measurements and instrumentation

Aerosol light scattering coefficients were measured every 5 min at three wavelengths (450, 525 and 635 nm) with a LED-based integrating nephelometer (model Aurora 3000, ECOTECH Pty, Ltd, Knoxfield, Australia).  $\sigma_{sp}$  Scattering  
25 measurements were ~~obtained for collected at~~ MSY ~~since 2010~~ using a PM<sub>10</sub> cut-off inlet. Measurements at MSA were carried out using a PM<sub>2.5</sub> cut-off inlet from 2011 until March 2014, and then replaced with a PM<sub>10</sub> cut-off inlet.  $\sigma_{sp}$  Scattering  
measurements at BCN ~~were are~~ not available. Calibration of the two nephelometers was performed three times per year using CO<sub>2</sub> as span gas, while zero adjusts were performed once per day using internally filtered particle free air. The relative humidity (RH) threshold was set following the ACTRIS-GAW recommendations (RH<40%). Scattering measurements  $\sigma_{sp}$   
30 coefficients were corrected for truncation due to non-ideal detection of scattered radiation following the procedure described in Müller et al. (2011ab).



Aerosol light absorption coefficient at 637 nm (Müller et al., 2011~~ba~~) was measured at 1 min resolution with a Multi Angle Absorption Photometer (MAAP, model 5012, Thermo), operated in the heated sampling mode and connected to a PM<sub>10</sub> cut-off inlet at BCN, MSY and MSA.

Gravimetric PM<sub>10</sub> mass concentrations were determined by standard gravimetric procedures, according to UNE-EN 12341, 1999 protocol (Alastuey et al., 2011). Samples were collected every 3 to 4 days on 150 mm quartz micro-fiber filters (Pallflex 2500 QAT-UP and Whatman QMH) using high-volume samplers (DIGITEL DH80 and/or MCV CAV-A/MSb at 30 m<sup>3</sup> h<sup>-1</sup>).

Chemical off-line filter analyses were carried out at the three sites following the procedure proposed by Querol et al. (2001). A quarter of the filter was acid digested (HNO<sub>3</sub>:HF:HClO<sub>4</sub>). The resulting solution was analyzed by Inductively Coupled

Plasma Atomic Emission Spectroscopy (ICP-AES; IRIS Advantage TJA Solutions THERMO) for the determination of major elements (Al, Ca, Fe, K, Na, Mg, S, Ti, P) and by Inductively Coupled Plasma Mass Spectrometry (ICP-MS; X Series II, THERMO) for the trace elements (Li, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Rb, Sr, Cd, Sn, Sb, Ba, rare earths, Pb, Bi, Th, U). In order to examine the accuracy of the acid digestion, a few milligrams of the reference material NIST 1633b were added to a quarter of the blank filter. Another quarter of each filter was water extracted to determine soluble anions. The

nitrate, sulfate and chloride concentrations were resolved by ~~Ion Chromatography (IC)~~ ion high-performance liquid chromatography (HPLC) using a WATERS ICpak<sup>TM</sup> anion column with a WATERS 432 conductivity detector, and the ammonium concentrations with an ion selective electrode (MODEL 710 A+, THERMO Orion). Organic carbon (OC) and EC concentrations were determined by a thermal-optical carbon analyzer (SUNSET) following the EUSAAR2 thermal protocol (Cavalli et al., 2010). Blank filters were analyzed together with the samples, and concentrations were subtracted from those found in the samples in order to calculate the ambient concentrations. Chemical filter analysis presented in this study ranges between the period 2004-2014 at BCN and MSY, and the period 2010-2014 at MSA. Optical measurements were considered for the periods ~~2009-2014~~ 2010-2014 at BCN, ~~2010-2014 at~~ MSY and 2011-2014 at MSA.

## **2.34 Positive Matrix Factorization model (PMF)**

The positive matrix factorization model (PMFv5.0, EPA) was individually applied ~~on-to~~ the daily chemical speciated data collected at BCN, MSY and MSA for source identification and apportionment ~~in-to~~ PM<sub>10</sub>. Source contributions obtained for BCN and MSY can be found in Pandolfi et al. (2016), whereas sources identified at MSA ~~will beare~~ presented in this study. Detailed information describing the PMF model can be found in literature (Paatero and Tapper, 1994; Paatero, 1997; Paatero and Hopke, 2003; Paatero et al., 2005).

Briefly, the PMF model is a factor analytical tool based on the weighted least-squares method, which reduces the dimension of the input matrix (i.e. the daily chemical speciated data) ~~in-to~~ a limited number of factors (or sources). Calculation of individual uncertainties and detection limits were based on the approach by Escrig et al. (2009) and Amato et al. (2009), where both the analytical uncertainties and the standard deviations of species concentrations in the blank filters were

considered in the uncertainties calculation. This procedure provides a criterion to separate the species which retain a significant signal from the ones dominated by noise, based on the signal-to-noise S/N ratio defined by Paatero and Hopke (2003). Species with  $S/N < 2$  ~~greater than 1 may often indicate good signal, though this depends on how uncertainties are determined, are generally defined as weak variables.~~ In order to avoid any bias in the PMF results the data matrix was uncensored, i.e. negative, zero and below detection limit values were included in the analyses.

The PMF was run in robust mode (Paatero, 1997) and rotational ambiguity was handled by means of the FPEAK parameter (Paatero et al., 2005). The final number of sources was selected based on several criteria: investigating the variation of the objective function Q (defined as the ratio between residuals and errors in each data value) depending on the number of sources (i.e. Paatero et al., 2002), studying the physical meaningfulness of factor profiles and contributions, and analyzing the scaled residuals and the G space plots.

## 2.4.5 Multilinear regression model (MLR)

~~Previous studies based on the IMPROVE algorithm have applied the m~~Multilinear regression (MLR) method ~~has been previously used in order to determine~~aiming to estimate the mass scattering and extinction efficiencies (MSE and MEE) of chemical species, ~~that correspond to the linear regression coefficients of the model~~ (White et al., 1986; de Vasconcelos et al., 2001; Hand and Malm, 2007). This kind of regression model between chemical species mass concentration and aerosol particle scattering or extinction coefficients thus assuming assumes an externally mixed aerosol. However, the apportionment of scattering by more than one species to the total scattering depends on the assumption of the internal or external mixing state of atmospheric aerosols, as already noted previous studies (White, 1986). Thus, assuming an internal mixing among chemical species that form a single variable in the regression equation will reduce the possible collinearity among the dependent variables of the MLR model, making at the same time the regression coefficients less sensitive to data uncertainties (Hand and Malm, 2007).As shown in the matrix correlation in Fig. S1, very low correlation was observed between pairs of aerosol sources identified with the PMF model at the three sites considered here.

~~In the present~~this study, we used the PMF source contributions ~~were considered~~ as dependent variables in the MLR model and the measured  $\sigma_{sp}$ scattering (Se) and  $\sigma_{ap}$ absorption (Abs) coefficients ~~were treated~~ as independent ones. Thus, the resulting regression coefficients of the model represent the MSE and MAE of mixed aerosol modes, given that the sources from PMF take into account the possible internal mixing among chemical species. Moreover, the MLR method assumes that all the species contributing to  $\sigma_{sp}$  and  $\sigma_{ap}$  are included in the equation. Thus, a better model performance is achieved here given that we used the full PM<sub>10</sub> chemical speciation in the PMF model for source identification and apportionment. As a result, a unique MSE and MAE can be obtained for each source. Following equations 1 and 2, the partial  $\sigma_{sp}$ scattering and  $\sigma_{ap}$ absorption contribution offor each source can be computed as the product between the source concentration contributions and the corresponding MSE/MAE, and t Then, total aerosol light  $\sigma_{sp}$ scattering and  $\sigma_{ap}$ absorption coefficients can be modeled as the sum of the scattering or absorption source contributions (Eq. 1 and 2).

$$\sigma_{sp} \sigma_{sc}^{\lambda}_{spPM_{10}} = \sum (MSE^{\lambda}_{source} \cdot [source]) \quad (\text{Equation 1})$$

$$\sigma_{ap} \sigma_{abs}^{\lambda}_{apPM_{10}} = \sum (MAE^{\lambda}_{source} \cdot [source]) \quad (\text{Equation 2})$$

The apportionment of scattering by more than one species to the total scattering depends on the assumption of the internal or external mixing state of atmospheric aerosols, as already noted previous studies using chemical species assuming an externally mixed aerosol (White, 1986). This study presents a different approach using the PM<sub>10</sub> source contributions as dependent variables in the MLR instead of chemical species concentrations for computing MSE and MAE. Thus, the resulting regression coefficients represent the scattering and absorption efficiencies of mixed aerosol modes given that the sources from PMF take into account the possible internal mixing. The assumption of an internal mixing among the different chemical species that form a single variable in the regression equation reduces some of the collinearity issues and makes the regression coefficients less sensitive to data uncertainties (Hand and Malm, 2007). Data collinearity due to meteorological fluctuations is also considered using the source contributions identified by PMF and then derived MSE and MAE are not biased by dispersion patterns. Actually, the matrix correlation showed in Fig. S1 demonstrates the low correlation presented between pairs of aerosol sources identified at MSA. Moreover, a better model perform is achieved taking into account the full chemical speciation used in the PMF for source apportioning, given that the MLR method assumes that all the species contributing to scattering and absorption are included in the equation.

It is remarkable should be considered that differences changes in the sampling conditions (i.e: RH or size cut-off) or differences in the chemical analysis methods used on sampled filters can influence the intensive optical properties (Delene and Ogren, 2002), and consequently the comparison among of the computed MSE and MAE resulting efficiencies obtained for different emplacements. The resulting efficiencies can be biased by the cut-off inlet, given that absorbing aerosols tend to be predominately in the sub-micron fraction (Andrews et al., 2011). In this study both  $\sigma_{sp}$  and  $\sigma_{ap}$  were collected using a PM<sub>10</sub> cut off inlet, thus guaranteeing uniformity among the performed particle optical measurements. An exception occurs at MSA, where a PM<sub>2.5</sub> cut-off inlet was used until March 2014 and then replaced by a PM<sub>10</sub> inlet. However, an estimation of the influence of the inlet change on the resulting MSE and MAE at MSA is difficult to achieve, given the relatively short  $\sigma_{sp}$  and  $\sigma_{ap}$  time series available thus preventing performing two different MLR analyses for the two fractions. In this study Moreover, scattering RH was controlled below 40% at MSY and MSA in order to minimize preventing the hygroscopic growth of the particles and then prevent a significant enhancement in the scattering efficiency, which could lead to an enhancement in the scattering efficiency. An overestimation of the An enhancement of the scattering or absorption efficiencies can also be due to the fact that the MLR is also related with the known bias in the MLR. This method tends to give more weight to those variables that are more accurately measured (such as sulfate), and conversely, underestimate the regression coefficients for species with larger uncertainty (organic matter) (White and Macias, 1987; Hand and Malm, 2007). In the present study, a comparison between modeled and measured coefficients was performed using

quantitative statistics. With this aim, the root mean square error (RMSE) and fractional bias (FB) ~~described in equation 3 (Ryan et al., 2005)~~, were computed for modelling evaluation. FB is described in Eq. 3 (Ryan et al., 2005), ~~where  $\sigma_{sp}^{sim}$~~  is the modeled scattering coefficient and  $\sigma_{sp}^{se}$  is the measured value, for each daily data point.

$$FB = \frac{\sigma_{sp}^{se^{sim}} - \sigma_{sp}^{se}}{\sigma_{sp}^{se}} \quad (\text{Equation 3})$$

A total of 303, 379 and 503 daily data points were used in the MLR analysis for source apportionment ~~analysis of~~ absorption at MSA, MSY and BCN, respectively. ~~Whereas 222 and 307 daily data points were considered for MSE calculation at MSA and MSY, ensuring that the number of samples is large enough to provide stable results.~~

## 2.56 Statistical tests for trends study

The Theil-sen slope estimate (TS) (Theil 1950; Sen 1968) is a non-parametric test which was investigated for the monthly averages of light scattering and absorption and SSA in order to test for the occurrence of a non-null slope in the data series during the period 2004-2014 at MSY. The total and annual reduction of these optical parameters was investigated using bootstrap resampling for the monthly deseasonalized time series, reducing the possible influence of outliers on trend estimates and obtaining robust slope p-values.

A multi-exponential fit ~~developed within the Task Force on Measurements and Modelling (TFMM) by the Meteorological Synthesizing Centre East (MSC-E) group (Shatalov et al., 2015), aimed to study at studying~~ temporal trends ~~of air pollution~~ in the multi-exponential form (Shatalov et al., 2015), was used for representing the decomposed modeled monthly temporal series in: main component, seasonal component and residual component. Additionally, this technique allowed us to estimate the non-linearity (NL) parameter for the trends. An NL of 10% was used as threshold to define a linear trend (NL<10%).

## 3. Results

### 3.1 Source profiles and contributions to PM<sub>10</sub>

Seven aerosol sources were identified at MSA in the PM<sub>10</sub> fraction by performing a PMF ~~model analysis for at the MSA station during~~ the period 2010-2014. The ~~source~~ chemical profiles and source contributions to the measured PM<sub>10</sub> mass are shown in Fig. 2 and Table 1. These results will be studied together with the Average absolute and relative chemical profiles (Fig. S2 ) and source contributions (Table 1) obtained for previously quantified by Pandolfi et al. (2016) at BCN and MSY for during the period 2004-2014, also considered in this study (Table 1), have been previously quantified by Pandolfi et al. (2016). Higher The highest PM<sub>10</sub> average concentrations ~~were was~~ found at the BCN urban station, followed, in this order, by the regional (MSY) and remote (MSA) background sites (34.0, 16.7 and 9.6  $\mu\text{g m}^{-3}$ , respectively), consistent with the progressive distance of the three stations from important emission sources.

On average, the most abundant sources contributing to PM<sub>10</sub> mass concentration levels at MSA were *Aged organics*, followed by *Mineral*, *Industrial/Traffic*, *Aged marine*, *AmmoniumSecondary sulfate*, *V-Ni bearing* and *AmmoniumSecondary nitrate*. *Aged organics* was mainly traced by OC and EC with maxima in summer, pointing to a large contribution from biogenic emission sources, and accounted for 2.8  $\mu\text{g m}^{-3}$  (29.4%) of the PM<sub>10</sub> mass concentration load. The internal mixing with EC internally mixed within this source suggests a clear anthropogenic contribution from combustion sources to this source despite the remote environment of MSA. However, the Aged organics source at MSA can be is considered to be dominated by secondary organic aerosols (SOA) arising from biogenic volatile organic compounds (VOCs) due to the predominance of OC in the chemical profile. Furthermore, it should also be considered the higher summer VOCs oxidative potential occurring in the Mediterranean which enhances SOA formation, due to both higher insolation and tropospheric ozone concentration, which enhance the OC concentrations (Fuzzi et al., 2006). This assertion is in agreement with previous studies deployed at MSA where SOA was found to be the foremost constituent of PM<sub>1</sub> organic aerosols (OA), especially in summer (90%) (Ripoll et al., 2015a). The Mineral source, which is traced by typical crustal elements such as Al, Ca, Mg, Fe, Ti, Rb and Sr, was related to both Saharan dust events and regional/local mineral contribution and accounted for an averaged PM<sub>10</sub> load contribution of 2.327  $\mu\text{g m}^{-3}$  (24.6%). The *Industrial/Traffic* source, is primarily traced by Pb, Zn, As, Sb, Cu and Ni, and contributed 1.109  $\mu\text{g m}^{-3}$  (11.3%). *Aged marine* source, is mainly traced mainly by Na and Cl, and in a minor proportion by Mg, SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup>, contributed 1.108  $\mu\text{g m}^{-3}$  (11.4%). *AmmoniumSecondary sulfate*, is a secondary inorganic source mainly traced mainly by SO<sub>4</sub><sup>2-</sup> and NH<sub>4</sub><sup>+</sup>, and Secondary nitrate, traced by NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> but also enriched in EC, contributed 0.987  $\mu\text{g m}^{-3}$  (9%) and 0.72  $\mu\text{g m}^{-3}$  (7%), respectively contributing 0.87  $\mu\text{g m}^{-3}$  (9.0%). V-Ni bearing source, is traced mainly by V, Ni and SO<sub>4</sub><sup>2-</sup>, and represented the direct emissions from heavy oil combustion, mainly shipping in the study area, and contributed contributing 0.879  $\mu\text{g m}^{-3}$  (8.2%) to the total PM<sub>10</sub>. Finally *Ammonium nitrate*, also secondary inorganic source, is traced by NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> and enriched in EC accounting for 0.72  $\mu\text{g m}^{-3}$  (7.5%) of the PM<sub>10</sub> load. Differently from BCN and MSY, the V-Ni bearing source at MSA was not enriched in EC possibly because of the high altitude of this station and its position, far from the NW Mediterranean coastline and shipping emissions. As summarized in Table 1, some common sources were identified at the three stations were: *Mineral*, *Aged marine*, *AmmoniumSecondary nitrate*, *AmmoniumSecondary sulfate* and, *V-Ni* and *Traffic* (at BCN) or the equivalent Industrial/Traffic (at MSY and MSA). The sources identified in BCN showed similar contributions, ranging from 10% to 17% of the total PM<sub>10</sub> mass concentration, except for the *Industrial* source (3%) given that most of the secondary industrial aerosols are apportioned to other secondary sources presented in this study. At BCN, sources traced by pollutants from anthropogenic activities were mostly are related to with fresh emissions from the Barcelona metropolitan area (i.e. *Traffic* and, *Road dust resuspension*), from the surrounding industrial zone (*Industrial*) and from vessel traffic shipping emissions from the harbor (*V-Ni*), presenting large contributions to PM<sub>10</sub>. However at MSY and MSA, both representatives of regional and remote backgrounds, pollutants were are transported together from the Barcelona urban and industrial areas thus resulting in an aged aerosol mixed with local pollutants.

A larger relative contribution of *Mineral* and *Aged organics* sources was observed at the MSA high-altitude site, MSA due to a less direct exposure to anthropogenic emissions. According to previous studies (Ripoll et al., 2015; Ealo et al., 2016), a higher relative *Mineral* contribution was found at MSA (24.6%) compared to MSY (16.2%) and, being relatively lower at BCN (14.6%). However, a higher absolute *Mineral* contribution mainly originated from local sources was observed at BCN ( $4.6 \mu\text{g m}^{-3}$ ), mainly originated from local origin. *Aged organics* also presented a higher relative contribution at the MSA remote site (29.37%) compared to MSY (23.7%). However, this source was not identified at BCN, where the *Traffic* source explained the majority of the measured OC. A larger absolute and relative contribution was found for the *Aged marine* source in Barcelona showed higher absolute and relative contributions ( $5.73 \mu\text{g m}^{-3}$ ; 176.9%) due to its proximity to the sea-coast, compared to MSY ( $1.876 \mu\text{g m}^{-3}$ ; 110.6%) and MSA ( $1.08 \mu\text{g m}^{-3}$ ; 11.4%). Higher relative contributions of *AmmoniumSecondary sulfate* and *AmmoniumSecondary nitrate* were found at MSY (24.7% and 87.9%) compared to MSA (9% and 7.5%), probably explained by likely because of the longer distance of the latter MSY to the Barcelona metropolitan nearby polluted area. Moreover, but also because of the free-troposphere conditions typically occurring in MSA during the colder period months, prevented the direct transport of aerosol particles from anthropogenic sources to the station, that prevent the emplacement from the influence of the main anthropogenic emissions. The *V-Ni bearing* source showed similar absolute contributions at MSY ( $0.7 \mu\text{g m}^{-3}$ ; 4.3%) and MSA ( $0.8 \mu\text{g m}^{-3}$ ; 8.2%) despite the longer distance of this latter MSA to the Mediterranean coast, pointing to a possible influence of long range transport at higher altitude affecting the mountain-top site. It should be noted that the current increasing shipping emissions are highly contributing to air quality degradation in coastal areas (Viana et al., 2014), but also in regional and remote environments as consequence of atmospheric transport processes.

A larger  $\text{PM}_{10}$  source contribution mostly related with anthropogenic activities was found at BCN due to the proximity to emission sources from the metropolitan, industrial and harbor areas. Conversely, the sources with higher contribution from natural processes, such as *Aged organics* and *Mineral*, were dominant at the regional and remote background sites. Therefore Overall, the impact of the identified aerosol sources at the pollutants at different background sites depended on the distance to important emission sources and on the aging and transport of aerosol particles to inland areas driven by orography and meteorology, thus mostly explaining the differences in the chemical profiles of the sources identified at the three sites, leading to differences in the source chemical profiles identified at the three sites. Thus, the larger the distance to emission sources the higher the aging and mixing ratio for those sources characterized by anthropogenic pollutants.

### 3.2 Seasonal variation of source contributions to $\text{PM}_{10}$

Monthly average source contributions to  $\text{PM}_{10}$  obtained at the three stations are shown in Fig. 3. MSY and MSA were characterized by presented a marked  $\text{PM}_{10}$  seasonal variation with higher concentrations in summer (June, July and August) and lower in winter (December, January, and February), in agreement with previous studies (Pérez et al., 2008 ; Ripoll et al., 2014). The summer increase is related with the higher frequency of Saharan dust events, the recirculation of air masses that

prevent air renovation, the re-suspension processes owing to the dryness of soils, the low precipitation and the formation of secondary aerosols enhanced by the maximum solar radiation (Rodriguez et al., 2002). The lower winter concentrations can be explained by the high frequency of Atlantic advections leading to a higher dispersion of pollutants and to higher precipitation rates, compared to summer. Moreover, the reduced contribution from the PBL in winter due to frequent thermal

inversions, also contributed to the relatively low PM<sub>10</sub> mass concentration at MSY, and especially at MSA (Pandolfi et al., 2014a) but also because of the free troposphere conditions affecting the stations, predominantly at the MSA mountain top site (Pandolfi et al., 2014). It is remarkable the PM<sub>10</sub> concentration peak observed in February and March at MSY, which might be attributed to the winter regional pollution episodes typical of the WMB (Pandolfi et al., 2014b). Such scenarios are characterized by anticyclonic conditions which favor the accumulation of pollutants close to the emission sources, and the subsequent transport of pollutants towards the station with the daily increase of the PBL. Pandolfi et al. (2014b) and Pey et al. (2010) reported high nitrate concentrations during these atmospheric conditions at MSY, in agreement with the increased contributions of *Secondary nitrate* shown in Fig. 3b during this time of the year period. The relatively low PM<sub>10</sub> concentration observed in August at BCN and MSY could be partially explained by reduced anthropogenic activities in the Barcelona metropolitan and industrial areas as a result of the holiday period in Spain. This result is supported by the minima absolute contributions observed in August for *Industrial* and *Traffic* sources at BCN (0.7 and 2.9  $\mu\text{g m}^{-3}$ , respectively) and for the *Industrial/Traffic* source at MSY (1.2  $\mu\text{g m}^{-3}$ ). The higher precipitation rates observed in August compared to June-July (Perez et al., 2008) might also contribute to reduce PM<sub>10</sub> concentrations at MSY. Conversely at MSA, the highest PM<sub>10</sub> concentration was observed in August probably due to the frequent Saharan dust events affecting the mountain top site, in accordance with the highest absolute contribution found for the *Mineral* source in August (3.9  $\mu\text{g m}^{-3}$ ).

Source contributions were proportionately distributed in BCN (10-17%), except for the *Industrial* source (3%) because most of the secondary industrial aerosols were apportioned to other secondary sources presented in this study. A notable increaseHigher relative contributions of *Aged marine* (23%), *Mineral* (18%) and *V-Ni bearing* (13%) sources is givenwere observed on average in summer at BCN. (June, July and August) as result of the sea breezes development, the higher frequency of Saharan dust events and the attendance of cruise ships in the Mediterranean sea during this season, respectively. By contrast, *Traffic* (23%), ~~*Ammonium*~~*Secondary nitrate* (21%) and *Industrial* (4%) sources maximized in winter (December, January, and February) (Fig. 3a). The seasonal variation of *Secondary sulfate* and *Secondary nitrate* can be attributed to a higher SOA contribution, the favored formation of sulfate, and the nitrate gas-aerosol partitioning leading to the thermal instability of *Secondary nitrate* during the warmer period, as was already observed in the area under study using off-line filter sampling (Pey et al., 2009; Ripoll et al., 2015b) and on-line measurements (Ripoll et al., 2015a). Differently from BCN,

A largerDifferently from BCN, a higher relative contribution of secondary sources, some of them with high natural contributionrelated with natural processes, was werefound observed at MSY and MSAthe rural and remote sites (3b and 3c). Increased contributions of *Secondary sulfate* were observed in summer (28.9% and 87.9% at MSY and MSA, repsectively).



whereas *Secondary nitrate* maximized in winter (17.3% and 110.9%). *Aged organics* showed the highest contribution in relative terms in winter (30% and 45% at MSY and MSA, respectively); however the highest absolute contributions were observed in summer (4.8 and 4.1  $\mu\text{g m}^{-3}$ ). This result is in agreement with the higher SOA formation found at MSA (Ripoll et al., 2015a) and MSY (Minguillón et al., 2015) during the warm period. *Aged organics* at MSA (29%) and *Ammonium sulfate* at MSY (24%) were the dominant sources throughout the year and reached the largest absolute contribution in summer. The *Mineral* source (19% and 27% at MSY and MSA, respectively) maximized in summer, although high contributions were also observed in spring. Similarly to BCN, *Aged marine* (14% and 13% for MSY and MSA, respectively) and *V-Ni bearing* (5% and 11%) sources showed the highest contribution in summer, whereas the *Industrial/Traffic* source maximized in winter (11% and 17%).

source also presented an important contribution in summer at both sites (29% and 27%), whereas *Ammonium nitrate* (17%) at MSY and the *Industrial/Traffic* (17%) at MSA increased during the colder period. *Ammonium nitrate* and *Ammonium sulfate* showed inverse seasonal trends, presenting this latter a higher mass contribution during the warm period. These seasonal variations can be attributed to a higher SOA contribution, the favoured formation of sulfate and the nitrate gas-aerosol partitioning leading to the thermal instability of *Ammonium nitrate* during the warmer period, as was already observed in previous studies using off line filter sampling (Pey et al., 2009; Ripoll et al., 2015) and on-line measurements (Minguillón et al., 2015; Ripoll et al., 2015).

### 3.3 Mass Scattering and absorption efficiencies of aerosol sources

Source dependent mass scattering efficiencies (at 450, 525 and 635 nm) at MSY and MSA and absorption efficiencies (at 637 nm) efficiencies obtained at the three different sites were obtained for the different sources identified by the PMF model are shown in (Table 2). The scattering and absorption efficiencies are the regression coefficients resulting from applying a MLR model between the concentration of the sources (dependent variables) and the scattering or absorption coefficients (independent variable) (Eq. 2).

The MSE and MAE for some of the sources reported in this study were not directly comparable to those coefficients MSE and MAE published in the literature for specific chemical species, given that the sources identified from PMF take into account the possible aerosol particle internal mixing. Similar MSE were observed for *Ammonium Secondary nitrate* at MSY and MSA ( $8.878 \pm 0.4$  and  $7.84 \pm 0.8 \text{ m}^2 \text{ g}^{-1}$  respectively, at 525 nm). These values were in the upper range when compared to other coefficients MSE found reported in the literature for ammonium nitrate chemical species calculated through stoichiometry the chemical compounds, highlighting the importance of taking into account the mixing state of atmospheric aerosols. Hand and Malm (2007) determined a MSE of  $3.2 \pm 1.2 \text{ m}^2 \text{ g}^{-1}$  for dry  $\text{PM}_{2.5}$  ammonium nitrate derived from stoichiometry; Cheng et al. (2015) obtained values of  $4.3 \pm 0.63 \text{ m}^2 \text{ g}^{-1}$  under high mass loading in China; and Titos et al. (2013) observed a coefficient of  $5 \pm 2 \text{ m}^2 \text{ g}^{-1}$  for nitrate ion in an urban area in southern Spain. MSE for *Secondary sulfate* were quite different between MSY and MSA ( $4.5 \pm 0.2$  and  $10.7 \pm 0.5 \text{ m}^2 \text{ g}^{-1}$ , respectively), probably due to differences in the



source origin and/or to the aging and mixing of ~~the contributions~~this source during the transport towards the stations. Hand and Malm (2007) ~~have~~ published lower values for the total mode of dry ammonium sulfate ranging between 0.83 and 2.4  $\text{m}^2 \text{g}^{-1}$ , whereas a ~~MSE coefficient~~ of  $3.5 \pm 0.5 \text{ m}^2 \text{g}^{-1}$  was found by Cheng et al. (2015) in a polluted environment. MSE for non-sea salt (nss) sulfate ion were calculated at Finokalia and Erdemli from the slope between total scattering and nss sulfate concentration, showing values of  $5.9 \pm 1.8$  and  $5.7 \pm 1.4 \text{ m}^2 \text{g}^{-1}$  respectively (Vrekoussis et al., 2005). Higher ~~MSE coefficients~~ were found in an urban background in the south of Spain (Titos et al., 2013) and ~~for in~~ the Negev desert (Formenti et al., 2001),  $7 \pm 1$  and  $7 \pm 2 \text{ m}^2 \text{g}^{-1}$  respectively. Given that in our study sulfate concentrations were mainly explained by ~~Ammonium~~Secondary sulfate and V-Ni sources, significant differences were also observed for the MSE of the V-Ni bearing source at MSY and MSA ( $8.0 \pm 1.5$  and  $3.5 \pm 0.5 \text{ m}^2 \text{g}^{-1}$ ). The V-Ni bearing source at MSY originated mainly from shipping emissions at regional (vessel traffic in the Mediterranean) and local (Barcelona harbor) scales. Conversely at MSA, located at higher altitude, this source ~~might be~~ also be influenced by continental transboundary transport and then internally mixed with different chemical species. In fact, as shown in Fig. 2 for MSA and in Fig. S2 for MSY, the V-Ni bearing source profile at MSA is enriched in OC which is not observed at MSY. The Aged marine source at MSA showed negative MSE at 525 and 635 nm. ~~This was likely possibly~~ due to the larger distance from the sea coast of MSA thus preventing a strong signal from the Aged marine source at this site, and/or due to the PM<sub>2.5</sub> cut-off inlet used at the beginning of the measurement period and also to the PM<sub>2.5</sub> cut-off inlet which prevented the sampling of coarse particles. However, ~~coefficients~~ MSE for the Aged marine source at MSY ( $1.24 \pm 0.32 \text{ m}^2 \text{g}^{-1}$ ) ~~showed~~exhibited values within the same range than those reported by Hand and Malm (2007) for coarse mode sea salt ( $1.0 \text{ m}^2 \text{g}^{-1}$ ). MSE for Aged organics ( $1.4 \pm 0.2$  and  $1.3 \pm 0.3 \text{ m}^2 \text{g}^{-1}$ ) and the Mineral sources ( $1.3 \pm 0.1$  and  $1.1 \pm 0.1 \text{ m}^2 \text{g}^{-1}$ ) was similar at MSY and MSA, ~~respectively, showed large similarity between both sites. This fact can be explained by the~~ This similarity could be explained by the low reactivity of common stability of this kind of mineral dust particles which were mostly externally mixed with other chemical species. Thus, less chemical transformation can be expected for mineral particles during the transport towards the stations..during the atmospheric transport, but also as a result of the similar source origin governed by same atmospheric processes. The Mineral source is mainly attributed to the transport of Saharan dust particles reaching the stations and local/regional dust re-suspension processes. Lower ~~coefficients~~ MSE were found for mineral matter ~~were shown~~ by Hand and Malm (2007) ( $0.7 \pm 0.2 \text{ m}^2 \text{g}^{-1}$ ), by Titos et al. (2013) in Granada urban background ( $0.2 \pm 0.3 \text{ m}^2 \text{g}^{-1}$ ) and by Vrekoussis et al. (2005) in Erdemli ( $0.2 \text{ m}^2 \text{g}^{-1}$ ). Similar coefficients were obtained by Vrekuossis et al. (2005) ~~for in~~ Finokalia ( $1 \text{ m}^2 \text{g}^{-1}$ ), and by Pereira et al. (2008) and Wagner et al. (2009) for mineral dust in Portugal,  $1 \pm 0.1 \text{ m}^2 \text{g}^{-1}$  and  $0.9 \text{ m}^2 \text{g}^{-1}$  respectively. ~~On the other hand, the~~ The MSE for the Aged organics source ( $1.4 \pm 0.2$  and  $1.3 \pm 0.3 \text{ m}^2 \text{g}^{-1}$ ) was also quite similar at MSY and MSA, respectively. probably due to similarities in the processes that govern the OA formation at both sites, which originated mainly from local/regional biogenic emissions and SOA formation (Minguillón et al., 2015; Ripoll et al., 2015a). The relatively low MSE of Aged organics compared to the MSE of other sources was probably due to the mixing of OA with EC in the source chemical profile (Fig. 2a and S2). Moreover, the possible presence of BrC in the measured OA could also explain the relatively low MSE. ~~originates from a mixture of local biogenic emissions and the transport of pollutants from the Barcelona area, giving~~

rise to an aged and mixed aerosol from regional/local origin. A low MSE is observed for *Aged organics* likely due to the EC contained within in the source. A similar ~~efficient~~ MSE ( $1.4 \text{ m}^2 \text{ g}^{-1}$ ) was reported by Hand and Malm (2007) for the total mode of primary organic matter (POM) ~~was reported by Hand and Malm (2007), whereas and a higher efficient MSE~~ ( $4.5 \pm 0.73 \text{ m}^2 \text{ g}^{-1}$ ) was found by Cheng et al. (2015) during a pollution episode in China. The *Industrial/Traffic* source showed similar ~~coefficients~~ MSE at MSY ( $2.1 \pm 0.8 \text{ m}^2 \text{ g}^{-1}$ ) and MSA ( $2.3 \pm 0.5 \text{ m}^2 \text{ g}^{-1}$ ). ~~This similarity was related to the common origin of this source at both sites (i.e. emission from the traffic and industrial activities). likely due to a common source origin affecting both sites from the Barcelona urban and industrial areas, where pollutants are transported to inland regions undergoing similar transformation processes.~~ It is remarkable that MSE for some of the sources identified in this work which highly contribute to air quality degradation, such as *Industrial/Traffic* or *V-Ni*, are not available in the literature.

Interestingly, ~~a higher scattering wavelength dependence was observed for those sources with higher contribution from anthropogenic tracers which are mainly present in the fine mode (Table 2). The specific Scattering Ångström Exponent (SAE) was obtained for each source as a linear fit of  $3\lambda$  scattering in the 450–635 nm range (Table 2). This parameter provide information on the size of the particles; generally a SAE lower than 1 or higher than 2 indicates that the scattering is dominated by larger or finer particles, respectively (Schuster et al., 2006). Aged organics and V-Ni sources showed the highest SAE at MSY (2.2 and 2.4) and MSA (3.6 and 2.2), respectively, pointing to a predominance of fine particles within these sources. Previous studies have demonstrated the strong contribution from shipping emissions to fine aerosols (Viana et al., 2009), and especially to ultrafine particles (Saxe and Larsen, 2004). Conversely, the lowest SAE was found for Mineral and Aged marine, which are mainly contained within the coarse fraction.~~

Prior studies ~~dealing with focusing on the~~ absorption efficiencies ~~of aerosol particles~~ mainly referred to BC particles and to the possible coating with non-absorbing material (Bond et al., 2013; Ramana et al., 2010). Other studies have reported the MAE of mineral matter (Linke et al., 2006) and OA (Lu et al., 2015; Updyke et al., 2012) due to the significant contribution of BrC to UV light absorption. However, ~~to the author's knowledge, this is the first time that absorption efficiencies, as well as scattering efficiencies, were computed for aerosol particle sources.~~ However, ~~to the author's knowledge, this is the first time that absorption efficiencies, as well as scattering efficiencies, are~~ computed for ~~different~~ aerosol ~~particle~~ sources, ~~aiming to study the relationship between the main contributors to air quality degradation and their potential to absorb the light.~~ MAE ~~coefficients values~~ at 637 nm for the three sites are summarized in Table 2. The highest absorption efficiencies were ~~found~~ ~~observed~~ for the *Traffic* source identified at BCN ( $1.672 \pm 0.050 \text{ m}^2 \text{ g}^{-1}$ ) and ~~for the equivalent~~ *Industrial/Traffic source* at MSY ( $0.867 \pm 0.047 \text{ m}^2 \text{ g}^{-1}$ ) and MSA ( $0.206 \pm 0.02 \text{ m}^2 \text{ g}^{-1}$ ), due to the internal mixing with BC particles from fossil fuel combustion. Interestingly, ~~the~~ *V-Ni bearing* source, which highly contributed ~~ds~~ to light scattering, also exhibited a high MAE at BCN ( $0.928 \pm 0.058 \text{ m}^2 \text{ g}^{-1}$ ) with decreasing coefficients at MSY ( $0.526 \pm 0.065 \text{ m}^2 \text{ g}^{-1}$ ) and MSA ( $0.165 \pm 0.017 \text{ m}^2 \text{ g}^{-1}$ ). ~~This source is progressively becoming more relevant for air quality due to the increased shipping emissions in recent years (Viana et al., 2014).~~ We have shown here that the *V-Ni bearing* source, which is progressively becoming more relevant for air quality degradation due to the increased shipping emissions in recent years (Viana et al., 2014), also has an important effect on light absorption as consequence of the internal mixing with combustion aerosols. ~~but also leads to an~~

important effect on light absorption as consequence of the internal mixing with combustion aerosols. The large MAE observed for *Secondary nitrate* at MSA ( $0.364 \pm 0.023 \text{ m}^2 \text{ g}^{-1}$ ) was due to the fact that this source explained around 20% of the measured EC concentration (Fig. 2a). A large MAE was observed for *Ammonium nitrate* at MSA ( $0.364 \pm 0.023 \text{ m}^2 \text{ g}^{-1}$ ), which explained around 20% of the measured EC concentration (Fig. 2a), compared to BCN and MSY ( $0.28 \pm 0.040$  and  $0.234 \pm 0.028 \text{ m}^2 \text{ g}^{-1}$ ) where this source presents a local and regional origin. Recently, Ripoll et al. (2015) have shown the increased concentration of nitrate, ammonium, EC and traffic/industrial tracers at MSA under European scenarios, when polluted air masses from central and eastern Europe are transported at higher altitude to the MSA site. Such scenarios are characterized by the transport of polluted air masses at high altitude from central and Eastern Europe to the MSA site. This fact may explain the internal mixing of BC particles in the chemical profile of *Secondary nitrate*, and consequently the higher absorption efficiency. MAE values found for this source *Ammonium nitrate* at this site MSA. Lower MAE for the *Secondary nitrate* source were observed at BCN and MSY ( $0.28 \pm 0.040$  and  $0.234 \pm 0.028 \text{ m}^2 \text{ g}^{-1}$ , respectively) compared to MSA. Lower MAE were found observed for *AmmoniumSecondary sulfate* ( $0.359 \pm 0.035$ ,  $0.122 \pm 0.010$  and  $0.173 \pm 0.021 \text{ m}^2 \text{ g}^{-1}$ ) at BCN, MSY and MSA, respectively). Overall, Higher absorption efficiencies were observed for the main anthropogenic sources at BCN, where fresh primary pollutants, mostly composed of darker particles, are emitted within the metropolitan, industrial and harbor areas. However, lower MAE were found determined for the same pollutant sources at MSY and MSA. This result pointing points to a decrease in the absorption efficiency towards inland areas, as a consequence of the mixing and aging of pollutants during the transport towards the stations. Aerosol sources dominated by natural contributions, such as *Aged marine and Mineral sources*, showed the lowest MAE at the three sites MSY and MSA. The *Road dust re-suspension* source found at BCN, which was partially composed by of mineral matter, exhibited the lowest MAE at BCN ( $0.062 \pm 0.084 \text{ m}^2 \text{ g}^{-1}$ ). The *Mineral* source presented the lowest MAE at BCN and MSY values of ( $0.09 \pm 0.05$ , and  $0.005 \pm 0.007 \text{ m}^2 \text{ g}^{-1}$ ) and, showing also low coefficients at MSA ( $0.03 \pm 0.003 \text{ m}^2 \text{ g}^{-1}$  at BCN, MSY and MSA). Coefficients in the same order of magnitude at 660 nm were found for the Sahara-Sahel and Gobbi deserts, ranging between 0.01 and  $0.02 \text{ m}^2 \text{ g}^{-1}$  (Alfaro et al., 2004), and for El Cairo and Morocco,  $0.02 \pm 0.004$  and  $0.06 \pm 0.014 \text{ m}^2 \text{ g}^{-1}$ , respectively (Linke et al., 2006). *Aged marine* also exhibited low absorption coefficients efficiencies at BCN, MSY and MSA ( $0.108 \pm 0.021$ ,  $0.027 \pm 0.018$  and  $0.015 \pm 0.010 \text{ m}^2 \text{ g}^{-1}$ , respectively), being larger higher at BCN due to a possible mixing with darker particles at urban level. Similarly to the results observed for MSE, *Aged organics* showed similar MAE at MSY and MSA ( $0.169 \pm 0.011$  and  $0.140 \pm 0.009 \text{ m}^2 \text{ g}^{-1}$ , respectively) due to the local/regional origin of this source with similar composition at both sites. The absorption efficiency of this latter source was mainly explained by the EC contained within the source chemical profile, but also might be partially due to the presence of light absorbing material detected as OC, such as brown carbon (Putaud et al., 2014).

### 3.3.1 SAE and SSA of aerosol sources

The source specific scattering Ångström exponents (SAE) were calculated as a linear fit of  $3\lambda$  MSE in the 450–635 nm range (Table 2). This parameter provides information on the size of the particles; generally a SAE lower than 1 or higher than 2

indicates that the scattering is dominated by large or fine particles, respectively (Schuster et al., 2006). *Aged organics* and *V-Ni* bearing sources showed the highest SAE at MSY (2.2 and 2.4, respectively) and MSA (3.6 and 2.2, respectively), pointing to a predominance of fine particles within these sources. Previous studies have demonstrated the strong contribution from shipping emissions to fine aerosols (Viana et al., 2009), and especially to ultrafine particles (Saxe and Larsen, 2004). As reported in Table 2, for both MSY and MSA, the SAE of *Secondary sulfate* (1.9 and 1.8, respectively) and *Secondary nitrate* (1.2 and 1.4, respectively) sources was lower compared to the SAE of the *Aged organics* source. This was probably due to the contribution of very fine primary organic aerosols (POA) to the *Aged Organic* source, whereas both SOA and secondary inorganic aerosols (SIA) are expected to strongly contribute to the accumulation mode (Sun et al., 2016). The lowest SAE was observed for *Mineral* (0.9 at MSY and MSA) and *Aged marine* (0.01 at MSY) sources, which primarily consist of coarse mode particles. A relatively low SAE was found for the *Industrial/Traffic* source (0.6 and 0.8 at MSY and MSA, respectively), which could be related to specific industrial processes in the area under study that include handling of dusty materials.

The single scattering albedo (SSA) coefficients obtained for each source at MSY are summarized in Table 2, and provide information on the relative importance of scattering or absorption in the light extinction process. The corresponding SSA to each source was computed as the ratio between the source specific MSE and the sum of MSE and MAE. As expected, the sources internally mixed with combustion particles, such as *Industrial/Traffic*, *Aged organics* and *V-Ni*, exhibited lower SSA, 0.74, 0.84 and 0.9, respectively. Conversely, *Aged marine* and *Mineral* sources showed the highest coefficients, 1 and 0.98, respectively, leading to a scattering dominance in the light extinction process. Accordingly to studies in the literature, the *Mineral* source showed a SSA close to 1. Linke et al. (2006) observed values around 0.98-0.99 at 532 nm, and lower coefficients were found by Müller et al. (2011c) for mineral dust (0.96) and marine (0.95) aerosols at 530 nm. Note that equivalent wavelengths should be considered when comparing SSA with coefficients in the literature, due to the strong wavelength dependence of mineral dust particles.

### 3.4 Seasonal variation of source contributions to scattering and absorption

Monthly source contributions to the total scattering and absorption coefficients are shown in Fig.3. The partial  $\sigma_{sp}$  scattering and  $\sigma_{ap}$  absorption apportioned to each source was calculated as the product between the aerosol source contribution and the corresponding MSE or MAE and the aerosol source concentration (Eq. 1 and 2). Accordingly to the scattering efficiencies previously reported in Table 2, average scattering for the whole period appears to be was mainly dominated by *AmmoniumSecondary sulfate* (356% and 335% at MSY and MSA, respectively) and *AmmoniumSecondary nitrate* (24% and 21%) at MSY (Figs. 3g and ) and MSA (Fig. 3h) respectively. The annual cycle of *AmmoniumSecondary sulfate* and *AmmoniumSecondary nitrate* scattering coefficients followed those of the PM<sub>10</sub> mass concentration, with maxima in summer (46% and 35% at MSY and MSA, respectively) and winter (42% and 29%) respectively, at MSY and MSA. Both sources presented inverse seasonal cycles following the seasonal variation of mass contributions, with *Ammonium sulfate*

maximizing in summer at MSY (46%) whereas showing similar contribution throughout the year at MSA. Conversely, *Ammonium nitrate* mainly governed the light scattering in winter (42% and 29% at MSY and MSA). The scattering contribution from Aged organics accounted for 11% and 16% of the total  $\sigma_{sp}$  at MSY and MSA, respectively. The *V-Ni bearing source* also exhibited substantial contribution to  $\sigma_{sp}$  scattering in summer (16%), despite the relative low mass contribution to  $PM_{10}$  mass concentration (5% and 10% at MSY and MSA, respectively). Less relevant were the scattering contributions of the other sources from *Industrial/Traffic* (6% and 11% at MSY and MSA, respectively) and *Mineral* (7%) sources, peaking in winter and summer, respectively.

The *Traffic* source at BCN and the *Industrial/Traffic* source at MSY clearly exerted the major influence on light absorption contributing 54% and 41% to  $\sigma_{ap}$ , respectively, despite the relative low  $PM_{10}$  contributions (16% and 10%, respectively). Maxima contributions were observed in winter at BCN for the *Traffic* source (65%) and in October-January at MSY for the *Industrial/Traffic* source (46%), whereas a lower influence of *Industrial/Traffic* was observed on average at MSA (18%) (Fig. 3 d, e, f).

Light absorption appeared to be almost dominated by the *Traffic* source at BCN and in a minor proportion by the equivalent *Industrial/Traffic* at MSY and MSA (Fig. 3d, e, f), showing high contributions in winter (65%, 42%, 22%) despite the relative low mass concentration (23%, 11%, 17%). Interestingly, the *V-Ni bearing source* also played an important role in the light absorption, especially in summer as a consequence of the increased vessel traffic reaching the maxima in summer, due to the increased cruise ships emissions in the Mediterranean but also because of the more intensive sea breezes circulations transporting pollutants to inland regions. Average contributions to  $\sigma_{ap}$  during this season in summer were 31% at BCN, 17% at MSY and around 16% at MSA. Therefore, *Traffic*, *Industrial/Traffic* and *V-Ni bearing* sources, which highly influenced air quality, also have caused also significantly contributed to  $\sigma_{ap}$ , important effect on radiative forcing, particularly and especially in those sites closer to the emission sources. *Aged organics* became a relevant source in the absorption process at the regional and remote continental background sites contributing (20% and 32%), respectively, due to both its large contribution to  $PM_{10}$  and its relatively large MAE compared to other sources. *AmmoniumSecondary sulfate* contributed on average by 10%, 16% and 12% to the total  $\sigma_{ap}$  at BCN, MSY and MSA, respectively, whereas *AmmoniumSecondary nitrate* showed an increasing contributions to  $\sigma_{ap}$  absorption towards inland areas (8%, 10% and 21%, respectively), markedly maximizing in winter, during the colder months.

As a summary, we have shown that the main target pollutant sources affecting air quality degradation have caused important effects on light extinction in the northwestern Mediterranean. Increasing absorption efficiencies were found for the main anthropogenic factors in areas closer to the emission sources, pointing that the aging and mixing state of aerosols resulting from the atmospheric transport and transformation processes are key factors influencing light absorption. Light absorption was mainly governed by the *Traffic* source at BCN followed by *V-Ni*. These sources at MSY and MSA were relevant in the light absorption process but not dominant, probably due to the mixing and aging of combustion pollutants during the transport towards the stations. *AmmoniumSecondary sulfate*, *AmmoniumSecondary nitrate* and *Aged organics* however, gained relative importance in the absorption process at MSY and MSA. Accordingly to the reviewed studies, light scattering

~~appeared to be dominated by AmmoniumSecondary sulfate and AmmoniumSecondary nitrate, in summer and winter respectively. As a novelty, V-Ni bearing source (mainly originated from shipping emissions) was also found to be an important contributor to scattering during summer, due to the internal mixing with sulfate particles.~~

### 5 3.5 Reconstruction of scattering and, absorption and SSA time series coefficients

Scattering ( $\sigma_{sp}$ ) and absorption ( $\sigma_{ap}$ ) time series were reconstructed by means of the sum of the partial scattering and absorption contributions determined for each source. ~~In this study, the partial scattering and absorption coefficients were obtained from the product between the daily source concentration and the specific MSE/MAE computed by means of the MLR (Eq. 1 and 2).~~

10 Strong correlations were found between the measured and modeled extensive optical parameters for the three sites the period 2010-2014 at BCN and MSY, and for the period 2011-2014 at MSA, when optical measurements were available (Fig. 4). Results showed good agreement for  $\sigma_{sp}$  scattering at 525 nm at MSY ( $R^2=0.88$ ) and MSA ( $R^2=0.92$ ).  $\sigma_{ap}$  Absorption at 637 nm also exhibited good correlation when by comparing measured and predicted coefficients at BCN ( $R^2=0.81$ ), MSY ( $R^2=0.80$ ) and MSA ( $R^2=0.93$ ). Slopes were close to one in all the cases and ranged between 0.96 and 0.98. These results are

15 consistent with the good agreement obtained in the MLR model for MSE and MAE calculation, ~~showing a~~  $R^2$  of 0.96 was obtained for all the cases, and ensuring the accuracy of the regression coefficients computed for each site. The root mean square error (RMSE) was calculated for the observed-modeled datasets, showing low dispersion and high accuracy in the modeled values. Scattering and absorption coefficients were well reproduced by the model, showing RMSE values of 8.76 and 6.06  $Mm^{-1}$  for  $\sigma_{sp}$  at MSY and MSA, and values of 2.61, 0.55 and 0.23  $Mm^{-1}$  for  $\sigma_{ap}$  at BCN, MSY and MSA, respectively. The fractional bias (FB) between ~~the~~ measured and predicted coefficients was obtained for each sampling site ~~was obtained~~ following equation 3. Results are shown in Fig. 5, where the FB is broken down by quintile from lowest to highest  $\sigma_{sp}$  scattering and  $\sigma_{sp}$  absorption values ~~(Ryan et al., 2005)~~. According to published results (Ryan et al. 2005 and references therein), a consistent overestimation was observed for all the modeled coefficients in the lower range of  $\sigma_{sp}$  scattering and  $\sigma_{ap}$  absorption, showing the highest bias in the 1<sup>st</sup> quintile. Biases were substantially reduced in the median

25 range values, whereas a minor underestimation was observed for the highest  $\sigma_{sp}$  scattering and  $\sigma_{ap}$  absorption values, 4<sup>th</sup> and 5<sup>th</sup> quintiles, with ~~a~~ negative FB. On average, a 3.8% and 5.6% overprediction was obtained for the modeled  $\sigma_{ap}$  absorption coefficients at MSY and BCN, using 503 and 375 daily data points in the analysis.  $\sigma_{sp}$  Scattering overprediction at MSY pointed to was 4% using 307 daily points, whereas However at MSA,  $\sigma_{sp}$  scattering and  $\sigma_{ap}$  absorption coefficients biased by 30.9% and 19.9% the observed values, considering 220 and 303 data points in the analysis. A larger overestimation of the

30 measured coefficients at MSA might be mainly explained mainly by the less number of daily chemical data used in the PMF model for the quantification of source contributions, but also because of the less number of scattering and absorption data points available for the MLR analysis.



An independent subset of the study period was considered, in order to further evaluate the PMF-MLR technique and the accuracy of the method to simulate optical properties when chemical source contributions were available. Therefore, a new PMF was performed in order to obtain the source contributions for the period 2004-2015 at MSY. With this aim, the simulation of  $\sigma_{sp}$  and  $\sigma_{ap}$  coefficients for the period January-December 2015 was carried out by means of the source specific MSE and MAE previously obtained in the MLR analysis for the period 2010-2014. Good agreement was found between modeled and measured  $\sigma_{sp}$  ( $R^2=0.85$ ) and  $\sigma_{ap}$  ( $R^2=0.76$ ) coefficients, at 525 and 637 nm respectively, showing slopes close to one for the year 2015 at MSY (Fig. 6). This analysis confirms the confidence of the PMF-MLR technique to accurately estimate  $\sigma_{sp}$  and  $\sigma_{ap}$  coefficients when chemical data is available.

As a result of the aforementioned sensitivity test, long-term time series of  $\sigma_{sp}$  scattering and  $\sigma_{ap}$  absorption were satisfactory reconstructed for the period 2004-2014 at BCN and MSY, and for the period 2011-2014 at MSA (Fig. 7), when  $PM_{10}$  chemical speciated data was available, for the period 2004-2014 at BCN and MSY and for the period 2011-2014 at MSA (Fig. 76).

The simulation of the SSA at MSY was obtained from the ratio between the modeled scattering (at 635 nm) and extinction coefficients (Fig. 7). In order to prevent biased results due to the low signal of the instruments during cleaner atmospheric conditions, only values higher than 1 and  $0.1 \text{ Mm}^{-1}$  for scattering and absorption coefficients, respectively, were considered in the SSA calculation. A higher uncertainty was found for the simulation of SSA compared to the extensive parameters (Fig. 4) with a  $R^2=0.43$ ; nevertheless slope was close to one. SSA values obtained for each source at MSY are summarized in Table 2 and provide information on the relative importance of scattering or absorption in the light extinction process. As expected, the sources internally mixed with combustion particles from anthropogenic activities such as *Industrial/Traffic*, *Aged organics* and *V-Ni* exhibited lower SSA, 0.74, 0.84 and 0.9 respectively. Conversely, *Aged marine* and *Mineral* sources showed the highest coefficients, 1 and 0.98 respectively, leading to a scattering dominance in the light extinction process. Accordingly to studies in the literature the *Mineral* source showed a SSA close to 1. Linke et al. (2006) showed values around 0.98-0.99 at 532 nm and lower coefficients were found by Müller et al. (2011) for mineral dust (0.96) and marine (0.95) aerosols at 530 nm. Note that equivalent wavelengths should be considered when comparing SSA mineral dust with coefficients in literature due to the strong wavelength dependence.

### 3.6 Long-term trends in scattering and absorption coefficients at MSY

The good agreement found between modeled and measured optical parameters allowed for the reconstruction of the scattering and absorption coefficients since 2004 at BCN and MSY and since 2010 at MSA (Fig. 6), when chemical speciation data was available. As a result, long-term trends of  $\sigma_{sp}$  and  $\sigma_{ap}$  optical parameters and their relationship with the trends of  $PM_{10}$  aerosol-source contributions can be investigated for an 11-year period at MSY (2004-2014). Despite a larger uncertainty was found for the modeled SSA, this technique allowed to further investigate the temporal trend of this important parameter and its relation with changes in atmospheric composition (Fig. 7). Temporal trends The trend of  $\sigma_{ap}$  at

BCN and MSA were not studied/evaluated due to the change in the location of the BCN sampling station in 2009 (Pandolfi et al., 2016), which affected mainly the contribution from the Traffic source, which was firstly installed close to a parking area until 2009 and then moved to an urban background. The short time series available for chemical species concentration composition at MSA makes made unfeasible the analysis of  $\sigma_{sp}$  and  $\sigma_{ap}$  trends at this station simulation of optical parameters for at least a 10-year period, and consequently also the trend study.

Temporal trends of the deseasonalized monthly averages for the modeled  $\sigma_{sp}$  and  $\sigma_{ap}$  at MSY were analyzed by means of the Theil Sen (TS) slope estimates for the modeled deseasonalized monthly averages of  $\sigma_{sp}$  and  $\sigma_{ap}$  coefficients optical parameters at MSY during for the period 2004-2014 are shown in (Table 3). The multi-exponential (ME) approach allowed to decompose  $\sigma_{sp}$  and  $\sigma_{ap}$  time series monthly time variation of absorption, scattering and SSA were decomposed in trend, main component, seasonal component and residual components using the multi-exponential (ME) method (Figure 8). Linear trends were identified for  $\sigma_{sp}$  and  $\sigma_{ap}$  all the studied variables, thus given that the non-linearly (NL) parameter was less than 10% (Shalaginov et al., 2015). Statistically significant decreasing trends were found for both  $\sigma_{sp}$  and  $\sigma_{ap}$  at MSY (Table 3) in all the cases.  $\sigma_{ap}$  Absorption at 637 nm has been reduced/decreased by  $-4.1 \% \text{ y}^{-1}$  ( $-0.16 \text{ Mm}^{-1} \text{ y}^{-1}$ ), whereas a decrease reduction of  $-4.6 \% \text{ y}^{-1}$  ( $-2.14 \text{ Mm}^{-1} \text{ y}^{-1}$ ) was obtained for  $\sigma_{sp}$  at 635 nm scattering, and v. Very similar trends were observed for  $\sigma_{sp}$  at 450 ( $-4.4 \% \text{ yr}^{-1}$ ) and 525 nm ( $-4.5 \% \text{ yr}^{-1}$ ) and 635 nm.

Accordingly to these results, decreasing trends were also observed for all the aerosol majority of the  $\text{PM}_{10}$  sources contributions identified at MSY during for the period 2004-2014, except for Aged organics and Aged marine sources (Pandolfi et al., 2016). A reduction in the absorption coefficient was/is directly related with the significant decreasing trends found by Pandolfi et al. (2016) for strong light-absorbing sources such as the Industrial/Traffic ( $-0.1 \mu\text{g m}^{-3} \text{ y}^{-1}$ ) and V-Ni bearing source ( $-0.07 \mu\text{g m}^{-3} \text{ y}^{-1}$ ). The observed However, scattering decreasing trends were probably could be mainly associated with a reduction in the contribution from those sources which scattered light more efficiently, i.e. AmmoniumSecondary sulfate and AmmoniumSecondary nitrate. In Pandolfi et al. (2016) these sources showed reduction rates of  $-6.27$  and  $-4.82 \% \text{ y}^{-1}$ , decreased by  $0.32$  and  $0.15 \mu\text{g m}^{-3} \text{ y}^{-1}$ , respectively, showing the highest reduction at MSY.

A marked decline was also observed for nitrate and sulfate particles/PM in other European monitoring sites since 1990, as outlined in the EMEP report 1/2016 (Colette et al., 2016), as outlined in the EMEP report 1/2016. Other studies have been published in the last years showing clearly that the concentrations of PM and other air pollutants, such as sulfur dioxide ( $\text{SO}_2$ ) and  $\text{NO}_2$  carbon monoxide ( $\text{CO}$ ), have markedly decreased during the last 15 years in many European countries (EEA, 2013; Barmpadimos et al., 2012; Cusack et al., 2012; Querol et al., 2014; among others).

Querol et al. (2014) and Pandolfi et al. (2016) investigated trends of PM chemical components and aerosol sources at MSY, providing further explanation on the causes leading to the reduction of the atmospheric pollutants in the area. The financial crisis affecting Spain from 2008 contributed to reduce the ambient PM concentrations. A decrease in AmmoniumSecondary nitrate can be explained by the reduction of ambient  $\text{NO}_x$  and  $\text{NH}_3$  concentrations (Querol et al., 2014). The decreasing trend of the Secondary sulfate source may be supported by the reduction of sulfate particles, mainly attributed to the gas desulfurization at several facilities (Pandolfi et al., 2016), as consequence of the lower energy consumption related with the



financial crisis and the associated decrease in  $\text{NO}_x$  emissions from the five power generation plants surrounding Barcelona. A reduction in  $\text{NO}_x$  concentrations is also related to a slight recession of the traffic density and therefore on road traffic emissions, as consequence of the financial crisis. A reduction in Ammonium sulfate resulted mainly from the decrease of secondary sulfate, which is mainly attributed to the EC Directive on Large Combustion Plants implemented in Spain from 2008, resulting in the flue gas desulfurization (FGD) at several facilities. A decrease in secondary sulfate may be also explained by the 75% reduction of  $\text{SO}_2$  concentration in the Barcelona harbor, supported by the regulation of sulfur content in shipping emissions in EU harbors from 2010 (Schembari et al., 2012). This regulation together with the 2007 ban around Barcelona on the use of heavy oils and petroleum coke for power generation, which contributed to a drastic decrease in V and Ni (Querol et al., 2014), were the main reasons supporting the observed reduction of the contribution of the *V-Ni bearing* source. A particular case is presented for *V-Ni*; this source was internally characterized by the internal mixing of secondary sulfate and combustion aerosols, and, as was already observed, consequently contributed simultaneously to both light scattering and absorption,  $\sigma_{\text{sp}}$  and  $\sigma_{\text{ap}}$ . Thus, the abatement strategies adopted in the recent years might have caused changes in the internal mixture of particles emitted from the *V-Ni bearing* source, and consequently in the contribution of this source to light extinction.

A reduction in *V-Ni* can be explained by the implementation of the 2008 regional air quality plan, in which the use of heavy oils and petroleum coke for power generation was forbidden around Barcelona in favour of natural gas. However, the enlarged and uncontrolled shipping emissions taking place in the last years might lead to an increase of the relative weight of shipping to the total of anthropogenic emissions (Viana et al., 2014), and therefore to the *V-Ni bearing* source. Hence, despite the observed reduction in *V-Ni*, the increasing shipping emissions might cause important changes in the internal mixture of this relevant source leading to changes in light extinction and thus which is becoming a key pollutant source to consider for climate assessment.

Interestingly, the SSA showed a significant decreasing trend of  $-0.11\% \text{ y}^{-1}$  ( $-0.001 \text{ yr}^{-1}$ ) leading to a total reduction (TR) of  $-1.24\%$  since 2004 at MSY, pointing that the atmosphere is getting significantly darker. A more significant decreasing trend on SSA was found by Putaud et al. (2014) from ground base measurements at dry conditions at 700 nm ( $-0.7\% \text{ y}^{-1}$ ) and from columnar measurements using sun photometer retrievals at 675 nm ( $-0.8\% \text{ y}^{-1}$ ) in the Po Valley. Differences in the SSA reduction at both sites might be explained by the severe pollution episodes taking place in the Po Valley resulting in a higher dominance of absorption in the light extinction process, compared to MSY which is representative of a less polluted environment.

Only few studies have been published in Europe aiming to study trends of particle optical properties. Statistically significant downward trends of PM mass concentration,  $\sigma_{\text{sp}}$ ,  $\sigma_{\text{ap}}$  and SSA were found in the Po valley (Italy) for the period 2004-2010 (Putaud et al., 2014). A higher decreasing rate was observed for  $\sigma_{\text{sp}}$  ( $-2.8\% \text{ yr}^{-1}$ ) compared to  $\sigma_{\text{ap}}$  ( $-1.1\% \text{ yr}^{-1}$ ), likely due to the increasing contribution of light-absorbing organic matter to light absorption during cold months in the Po Valley (Putaud et al., 2014). In the present study, smaller differences between  $\sigma_{\text{sp}}$  and  $\sigma_{\text{ap}}$  were observed at MSY, accounting the total

reduction trends for -50% and -45%, respectively. This fact might be explained by the different background sites considered; whereas the Po Valley is a highly polluted area, MSY is representative of a cleaner environment where biomass burning emissions, which highly contribute to light absorption, are considerably lower (Minguillón et al., 2015; Ealo et al., 2016).

Several facts might have accounted for a decreasing trend in the SSA at MSY since 2004; the air quality policies implemented in the last years were very effective in reducing the atmospheric concentration of aerosol species sources with large scattering efficiency (cooling effect), leading to a scattering TR of -52% since 2004. However, abatement strategies focused on reducing pollutants containing dark particles (mainly emitted from fossil fuel combustion sources) were less effective, leading to a less pronounced TR of -44% in the  $\sigma_{\text{ap}}$  absorption coefficient. This fact resulted in the enhancement of the relative weight of absorption, therefore contributing to diminish the SSA. It should also be considered that the reduction of the primary energy consumption and industrial activities related to the financial crisis affecting Spain since 2008 contributed to the decrease of the ambient concentration of pollutants (Querol et al., 2014), and consequently to the reduction of light scattering and absorption. Another fact to be considered is the increasing use of commercial and domestic biomass burning system in most European countries (Kirehstetter, 2004). Putaud et al. (2014) found that an increase in the contribution of light absorbing organic matter, from biomass burning emissions, to light absorption during cold months could be an explanation for the decrease in SSA in the Po Valley. A reduction in the SSA at MSY might be partially explained by a more significant decrease in the sources scattering light more efficiently, which could have helped to unmask the contribution of biomass burning to light absorption. Minguillón et al. (2015) and Ealo et al. (2016) found that winter biomass burning emissions at MSY present an important contribution to both ambient air BC and organic aerosols (OA) concentrations. This fact, together with the observed increasing trend for *Aged organics* (Pandolfi et al., 2016), might partially explain a less pronounced decreasing trend in the absorption coefficient contributing to reduce the SSA.

The reduction in the SSA trend points out the increasing prominence of absorption in the light extinction process in the NW Mediterranean. The decrease in the atmospheric PM load was thought to be beneficial for air quality and health; however the resulting reduction of light scattering aerosols lead to an increase of the incoming solar radiation contributing to climate warming. This radiative forcing is enhanced by the less effectiveness of the air quality policies focused on reducing pollutants containing BC particles, which highly contribute to light absorption. Therefore, the heterogeneous and non-selective reduction of pollutant sources, showing opposite effects on radiative forcing, may cause important changes on the temporal trends of optical properties, and therefore on the earth-atmosphere radiative balance. win-win regulation strategies which should be focused on both air quality and climate, and not acting separately. Given the high  $\text{PM}_{10}$  concentration, the toxicity of their chemical tracers and the contribution to light absorption in the NW Mediterranean, *Industrial/Traffic* and *V-Ni bearing* are target sources which should be abated for preventing health disorders, improving air quality and mitigate climate warming.

Further research on light scattering and absorption long-term trends and its relation with changes in atmospheric composition is needed to better understand the role of aerosols on optical properties and on the climate system. Based on the published studies and the present results, further efforts focusing on the reduction of atmospheric pollutants containing BC particles

(mainly emitted from fossil fuel combustion and biomass burning sources) need to be addressed. Given the toxicity of their chemical tracers, as well as their large contribution to light absorption, *Industrial/Traffic* and *V-Ni bearing* sources must be reduced through the implementation of win-win policies, aiming to improve air quality and public health, and mitigate climate warming.

#### 4. Summary and conclusions

Mass scattering and absorption efficiencies (MSE and MAE) of different aerosol particle sources were investigated at urban, regional and remote backgrounds in the NW Mediterranean, using unique large datasets of PM<sub>10</sub> chemical speciation and particle optical properties. ~~With this aim~~For this purpose, a new approach was presented aiming to apportion the PM<sub>10</sub> source contributions, arising from a PMF model, to the measured particle  $\sigma_{sp}$  and  $\sigma_{ap}$  coefficients, ~~developed for scattering and absorption source apportionment considering the aerosol source contributions, arising from a positive matrix factorization (PMF) analysis, as dependent variables in a Multilinear Regression (MLR) model for MSE and MAE calculation.~~

Seven aerosol sources were identified at the Montsec (MSA) ~~remote~~-mountain-top site, where *Aged organics* (29.4%) was the foremost constituent of PM<sub>10</sub>, followed by *Mineral* (24.6%), *Industrial/Traffic* (11.3%), *Aged marine* (11.4%), *AmmoniumSecondary* sulfate (9%), *V-Ni bearing* (8.2%) and *AmmoniumSecondary* nitrate (7.5%). ~~The same sources have been identified~~found at Montseny (MSY) regional background, showing the secondary aerosol sources a higher relative PM<sub>10</sub> ~~concentration~~ contributions at the background sites than at the Barcelona (BCN) urban station. ~~load at these background sites. At the Barcelona (BCN) urban background site~~*Aged organics* was not identified at BCN; however specific pollutant sources related to the direct anthropogenic emissions (~~*Traffic*, *Industrial/metallurgy* and *Road-resuspension*~~) were isolated (*Traffic*, *Industrial/metallurgy* and *Road-resuspension*). ~~Some of the anthropogenic sources identified at MSY and MSA, such as *Industrial/Traffic*, resulted from the internal mixture between local aerosols and pollutants transported from the BCN industrial and metropolitan area. We have found that~~The impact of aerosol sources and the different ~~changing~~ chemical profiles obtained at the three different ~~background~~ sites depended on the distance and transport of pollutants to inland areas, driven by orography and meteorology.

The highest absorption efficiencies were attributed to aerosol sources internally mixed with BC particles. ~~The *Traffic* source at BCN (MAE=1.7 m<sup>2</sup> g<sup>-1</sup>) at BCN and the equivalent mixed *Industrial/Traffic* source at MSY and MSA (MAE=0.87 and 0.2 m<sup>2</sup> g<sup>-1</sup>) mainly governed~~exerted the major influence on light absorption ~~in the NW Mediterranean, and reached the highest contributions during the colder period (65% and 46%, respectively).~~with increasing contributions in winter by 54%, 40% and 18%, respectively. The *V-Ni bearing* source was the second most efficient light-absorbing source in BCN (MAE=0.93 m<sup>2</sup> g<sup>-1</sup>), showing also a notable absorption efficiency at MSY and MSA (0.53 and 0.16 m<sup>2</sup> g<sup>-1</sup>, respectively). This source ~~originated mainly from shipping emissions and~~highly contributed in summer to both  $\sigma_{sp}$  scattering (around 16% at ~~the background sites~~MSY and MSA) and  $\sigma_{ap}$  ~~absorption~~ (31%, 17% and 16% at BCN, MSY and MSA, respectively) ~~during~~

summer, due to the simultaneous internal mixing of sulfate and combustion aerosols. These combustion sources were relevant but not dominant at MSY and MSA, where secondary aerosol sources (*AmmoniumSecondary sulfate*, *AmmoniumSecondary nitrate* and *Aged organics*) gained relative importance in the light extinction process. *Aged organics* contributed on average to absorption by 20% and 32% at MSY and MSA. *AmmoniumSecondary nitrate* showed increasing contributions in winter, accounting for 11%, 17% and 21% of the total absorption at BCN, MSY and MSA. A high spatial variability of MAE was observed for most of the anthropogenic sources, from high values at the BCN site to decreasing coefficients at the background stations, pointing to the aging and mixing state of aerosols as key factors influencing light absorption. The highest scattering efficiencies were found for *AmmoniumSecondary sulfate* (4.5 and 10.7 m<sup>2</sup>g<sup>-1</sup> at MSY and MSA, respectively), *AmmoniumSecondary nitrate* (8.8 and 7.8 m<sup>2</sup>g<sup>-1</sup>) and *V-Ni bearing* (8 and 3.5 m<sup>2</sup>g<sup>-1</sup>) sources at MSY and MSA respectively, dominating the scattering throughout the year with marked seasonal trends. *AmmoniumSecondary nitrate* highly contributed in winter by (42% and 29% at MSY and MSA, respectively); whereas in summer *Secondary sulfate* (46% and 35%) was the main contributor to scattering. was mainly governed by *Ammonium sulfate* (46% and 35%).

Sources internally mixed with relatively dark and fine particles and highly contributing to light absorption, such as *Industrial/Traffic*, *Aged organics* and *V-Ni*, were simultaneously characterized with low single scattering albedo (SSA) and high scattering Ångström exponent (SAE). Conversely, *Mineral* and *Aged marine* showed the highest-lowest SAE and the lowest-highest SSA, being scattering the dominant process in the light extinction. These findings for the intensive parameters were consistent at MSY and MSA. The observed variability of these intensive optical properties of aerosol sources provides as a function of both chemical composition and emissions sources is a valuable constraints for future simulations of aerosol parameters information that could help to constrain model estimates of aerosol parameters.

Significant decreasing trends were observed for the modeled scattering (-4.6 % y<sup>-1</sup>) and absorption (-4.1 % y<sup>-1</sup>) series at MSY for the period 2004-2014. The scattering reduction was mainly attributed to the decrease of the contributions from *Secondary nitrate*, *Secondary sulfate* and *V-Ni bearing* sources, whereas the absorption decreasing trend was mainly related to the decrease of *Industrial/Traffic* and *V-Ni bearing* sources. Given the toxicity of their chemical tracers, as well as the large contribution to light absorption, further efforts need to be addressed to reduce aerosol sources containing combustion particles, such as *Industrial/Traffic* and *V-Ni bearing* sources. Further studies focusing on the study of long-term trends of optical parameters and their relationship with changes in atmospheric composition are needed to assess future win-win mitigation strategies.

Significant decreasing trends were observed for the modeled scattering (-4.6 % y<sup>-1</sup>), absorption (-4.1 % y<sup>-1</sup>) and SSA (-0.11 % y<sup>-1</sup>) time series during 2004-2014 at MSY. A total reduction (TR) of 1.12% in the SSA was mainly motivated by the heterogeneous and non-selective reduction of key aerosol sources showing opposite effects on radiative forcing. Abatement strategies aimed at reducing atmospheric PM were thought to be beneficial for air quality and health. However, these measures have resulted in a more pronounced reduction of light scattering aerosol sources (*Ammonium nitrate*, *Ammonium sulfate*), leading to an increase of the incoming solar radiation and therefore contributing to climate warming. This positive

radiative effect is enhanced by the less effectiveness of air quality strategies for reducing light absorbing sources containing dark particles. A decrease in the SSA trend points to a darkening of the atmosphere and consequently to a progressive predominance of absorption in the light extinction process in the NW Mediterranean.

The author's would like to highlight (The new Findings and main advantages offrom the PMF-MLR technique are summarized as follows, summarized as follows. This study can be reproduced in other emplacements with available large chemical data sets in order to further research the role of aerosol sources on light extinction, contributing to reduce uncertainties in climate forcing.

- The apportionment of PM source contributions to scattering and absorption allows the determination of MSE and MAE of atmospheric aerosol sources, taking into account the particle internal mixing.

- The knowledge of both MSE and MAE gives the possibility to study the relationship existing between the sources contributing to air quality degradation and their potential to absorb and scatter visible light. Anthropogenic sources such as *Secondary sulfate*, *Secondary nitrate*, *Traffic*, *Industrial/Traffic* and *V-Ni bearing source*, which highly contribute to air quality degradation, also revealed a substantial contribution to light extinction in the NWM.

- To the author's knowledge, this work quantifies for the first time the absorption efficiency exerted by the different aerosol sources constituting the  $PM_{10}$  mass concentration, differently from previous studies where light absorption was entirely attributed to BC particles. Interestingly, secondary sulfate, secondary nitrate and organic aerosols, which light-absorbing properties are poorly represented in current climate models, significantly contributed to light absorption due to the internal mixing with BC or BrC particles, and especially at regional and remote levels.

- The proposed approach allowed a satisfactory reconstruction of  $\sigma_{sp}$  and  $\sigma_{ap}$  compared to previous studies, given that the sum of the source contributions used in the MLR model reached around 100% of the measured  $PM_{10}$  mass concentration. Correlation coefficients are higher than 0.8 with slopes close to 1.0 between modeled and measured  $\sigma_{sp}$  and  $\sigma_{ap}$ .

- Statistically significant decreasing trends were observed for the modeled  $\sigma_{sp}$  and  $\sigma_{ap}$  series, mirroring the effectiveness of the mitigation strategies adopted to improve air quality. The simultaneous analysis of the trends of climate relevant aerosols parameters ( $\sigma_{sp}$  and  $\sigma_{ap}$ ) together with the trends of PM source contributions allowed studying the effects that the abatement strategies implemented in the last years are having on atmospheric composition and light extinction.

- Using aerosol source contributions in the MLR model allows for a comprehensive performance of the chemical speciation in the apportionment to scattering and absorption, taking into account the internal mixing state of atmospheric aerosols and therefore achieving a more realistic proxy for MSE and MAE coefficients.

- Scattering and absorption efficiencies for target pollutant sources, highly contributing to air quality degradation, also revealed a substantial contribution to light extinction in the NW Mediterranean, thus leading to directly linking the air quality and climate effects of airborne particle matter. To the author's knowledge, this is the first time that light absorption is apportioned to different emission sources, compared to previous studies where it is entirely attributed to BC particles.

~~A consistent improvement in the reconstruction of scattering coefficients was achieved regarding previous studies. Correlation coefficients were higher than 0.8 with slopes close to 1.0 between modeled and measured scattering and absorption. The number of daily data used in the PMF and MLR models was found to be a limiting factor in the performance of the analysis, resulting in under and overestimation for the low and high scattering and absorption coefficient values, respectively.~~

~~Scattering, absorption and single scattering albedo (SSA) time series were reconstructed since 2004 based on the PM<sub>10</sub> source contribution data and MSE and MAE regression coefficients. As a result, a long term trend study was performed for these climate relevant parameters, allowing to further research on the effects that atmospheric pollutants and the abatement strategies implemented in the last years are causing on atmospheric composition and light extinction.~~

## Acknowledgements

15 This work was supported by the MINECO (Spanish Ministry of Economy and Competitiveness) and FEDER funds under the PRISMA project (CGL2012-39623-C02/00), by the MAGRAMA (Spanish Ministry of Agriculture, Food and Environment) and by the Generalitat de Catalunya (AGAUR 2014 SGR33 and the DGQA). This work has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 654109. Marco Pandolfi is  
20 funded by a Ramón y Cajal Fellowship (RYC-2013-14036) awarded by the MINECO. The authors would like to express their gratitude to D. C. Carslaw and K. Ropkins for providing the OpenAir software used in this paper (Carslaw and Ropkins, 2012; Carslaw, 2012).

## Data availability

The Montseny and Montsec data sets used for this publication are accessible online on the WDCA (World Data Centre for Aerosols) web page: <http://ebas.nilu.no>. The Barcelona data sets were collected within different national and regional  
25 projects and/or agreements and are available upon request.

## References

## References

Alastuey, A., Minguillón, M. C., Pérez, N., Querol, X., Viana, M., and de Leeuw, F.: PM10 measurement methods and correction factors: 2009 status report, ETC/ACM Technical Paper 2011/21, 2011.

30 Alfaro, S. C., Lafon, S., Rajot, J. L., Formenti, P., Gaudichet, A. and Maillé, M.: Iron oxides and light absorption by pure

- desert dust: An experimental study, *J. Geophys. Res.*, 109(D8), D08208, doi:10.1029/2003JD004374, 2004.
- Amato, F., Pandolfi, M., Escrig, A., Querol, X., Alastuey, A., Pey, J., Perez, N. and Hopke, P. K.: Quantifying road dust resuspension in urban environment by Multilinear Engine: A comparison with PMF2, *Atmos. Environ.*, 43(17), 2770–2780, doi:10.1016/j.atmosenv.2009.02.039, 2009.
- 5 Andrews, E., Ogren, J. A., Bonasoni, P., Marinoni, A., Cuevas, E., Rodríguez, S., Sun, J. Y., Jaffe, D. A., Fischer, E. V., Baltensperger, U., Weingartner, E., Coen, M. C., Sharma, S., Macdonald, A. M., Leaitch, W. R., Lin, N.-H., Laj, P., Arsov, T., Kalapov, I., Jefferson, A. and Sheridan, P.: Climatology of aerosol radiative properties in the free troposphere, *Atmos. Res.*, 102(4), 365–393, doi:10.1016/j.atmosres.2011.08.017, 2011.
- Barnpadimos, I., Keller, J., Oderbolz, D., Hueglin, C. and Prévôt, A. S. H.: One decade of parallel fine (PM<sub>2.5</sub>) and coarse  
 10 (PM<sub>10</sub>–PM<sub>2.5</sub>) particulate matter measurements in Europe: trends and variability, *Atmos. Chem. Phys.*, 12(7), 3189–3203, doi:10.5194/ACP-12-3189-2012, 2012.
- Belis, C. A., Karagulian, F., Larsen, B. R. and Hopke, P. K.: Critical review and meta-analysis of ambient particulate matter source apportionment using receptor models in Europe, *Atmos. Environ.*, 69, 94–108, doi:10.1016/j.atmosenv.2012.11.009, 2013.
- 15 Bond, T. C., Doherty, S. J., Fahey, D. W., Forster, P. M., Berntsen, T., Deangelo, B. J., Flanner, M. G., Ghan, S., Kärcher, B., Koch, D., Kinne, S., Kondo, Y., Quinn, P. K., Sarofim, M. C., Schultz, M. G., Schulz, M., Venkataraman, C., Zhang, H., Zhang, S., Bellouin, N., Guttikunda, S. K., Hopke, P. K., Jacobson, M. Z., Kaiser, J. W., Klimont, Z., Lohmann, U., Schwarz, J. P., Shindell, D., Storelvmo, T., Warren, S. G. and Zender, C. S.: Bounding the role of black carbon in the climate system: A scientific assessment, *J. Geophys. Res. Atmos.*, 118(11), 5380–5552, doi:10.1002/jgrd.50171, 2013.
- 20 Cavalli, F., Viana, M., Yttri, K. E., Genberg, J. and Putaud, J.-P.: Toward a standardised thermal-optical protocol for measuring atmospheric organic and elemental carbon: the EUSAAR protocol, *Atmos. Meas. Tech.*, 3(1), 79–89, doi:10.5194/amt-3-79-2010, 2010.
- Chen, L., Shi, G., Qin, S., Yang, S. and Zhang, P.: Direct radiative forcing of anthropogenic aerosols over oceans from satellite observations, *Adv. Atmos. Sci.*, 28(4), 973–984, doi:10.1007/s00376-010-9210-4, 2011.
- 25 Cheng, Z., Jiang, J., Chen, C., Gao, J., Wang, S., Watson, J. G., Wang, H., Deng, J., Wang, B., Zhou, M., Chow, J. C., Pitchford, M. L. and Hao, J.: Estimation of aerosol mass scattering efficiencies under high mass loading: case study for the megacity of Shanghai, China., *Environ. Sci. Technol.*, 49(2), 831–8, doi:10.1021/es504567q, 2015.
- Collaud Coen, M., Andrews, E., Asmi, a., Baltensperger, U., Bukowiecki, N., Day, D., Fiebig, M., Fjaeraa, a. M., Flentje, H., Hyvärinen, a., Jefferson, a., Jennings, S. G., Kouvarakis, G., Lihavainen, H., Lund Myhre, C., Malm, W. C.,

- Mihapopoulos, N., Molenaar, J. V., O'Dowd, C., Ogren, J. a., Schichtel, B. a., Sheridan, P., Virkkula, a., Weingartner, E., Weller, R. and Laj, P.: Aerosol decadal trends-Part 1: In-situ optical measurements at GAW and IMPROVE stations, *Atmos. Chem. Phys.*, 13, 869–894, doi:10.5194/acp-13-869-2013, 2013.
- Colette et al., 2016. Air pollution trends in the EMEP region between 1990 and 2012. Joint Report of the EMEP Task Force on Measurements and Modelling (TFMM), Chemical Co-ordinating Centre (CCC), Meteorological Synthesizing Centre-East (MSC-E), Meteorological Synthesizing Centre-West (MSC-W). Kjeller, NILU (EMEP: TFMM/CCC/MS-C-E/MS-C-W Trend Report) (EMEP/CCC, 01/2016).
- Cusack, M., Alastuey, a., Pérez, N., Pey, J. and Querol, X.: Trends of particulate matter (PM 2.5) and chemical composition at a regional background site in the Western Mediterranean over the last nine years (2002-2010), *Atmos. Chem. Phys.*, 12, 8341–8357, doi:10.5194/acp-12-8341-2012, 2012.
- Dall'Osto, M., Querol, X., Alastuey, A., O'Dowd, C., Harrison, R. M., Wenger, J. and Gómez-Moreno, F. J.: On the spatial distribution and evolution of ultrafine particles in Barcelona, *Atmos. Chem. Phys.*, 13(2), 741–759, doi:10.5194/acp-13-741-2013, 2013.
- Delene, D. J. and Ogren, J. A.: Variability of aerosol optical properties at four North American surface monitoring sites, *J. Atmos. Sci.*, 59(6), 1135–1150, 2002.
- Ealo, M., Alastuey, A., Ripoll, A., Pérez, N., Minguillón, M. C., Querol, X., and Pandolfi, M.: Detection of Saharan dust and biomass burning events using near-real-time intensive aerosol optical properties in the north-western Mediterranean, *Atmos. Chem. Phys.*, 16, 12567-12586, doi:10.5194/acp-16-12567-2016, 2016.
- EEA: European Environmental Agency Air quality in Europe — 2013 report, EEA report 9/2013, Copenhagen, 1725-9177 (2013) [107 pp. <http://www.eea.europa.eu/publications/air-quality-in-europe-2013>].
- Escrib Vidal, A., Monfort, E., Celades, I., Querol, X., Amato, F., Minguillón, M. C., and Hopke, P. K.: Application of optimally scaled target factor analysis for assessing source contribution of ambient PM10, *J. Air Waste Manage.*, 59, 1296–1307, 2009.
- Escudero, M., Querol, X., Ávila, A. and Cuevas, E.: Origin of the exceedances of the European daily PM limit value in regional background areas of Spain, *Atmos. Environ.*, 41(4), 730–744, doi:10.1016/j.atmosenv.2006.09.014, 2007.
- Formenti, P., Andreae, M. O., Andreae, T. W., Ichoku, C., Schebeske, G., Kettle, J., Maenhaut, W., Cafmeyer, J., Ptasiński, J., Karnieli, A. and Lelieveld, J.: Physical and chemical characteristics of aerosols over the Negev Desert (Israel) during summer 1996, *J. Geophys. Res. Atmos.*, 106(D5), 4871–4890, doi:10.1029/2000JD900556, 2001.



- Fuzzi, S., Andreae, M. O., Huebert, B. J., Kulmala, M., Bond, T. C., Boy, M., Doherty, S. J., Guenther, A., Kanakidou, M., Kawamura, K., Kerminen, V.-M., Lohmann, U., Russell, L. M. and Pöschl, U.: Critical assessment of the current state of scientific knowledge, terminology, and research needs concerning the role of organic aerosols in the atmosphere, climate, and global change, *Atmos. Chem. Phys.*, 6(7), 2017–2038, doi:10.5194/acp-6-2017-2006, 2006.
- 5 Hand, J. and Malm, W. C.: Review of the IMPROVE Equation for Estimating Ambient Light Extinction Coefficients, Cooperative Institute for Research in the Atmosphere. Available at: [http://vista.cira.colostate.edu/IMPROVE/Publications/GrayLit/016\\_IMPROVEeqReview/IMPROVEeqReview.htm](http://vista.cira.colostate.edu/IMPROVE/Publications/GrayLit/016_IMPROVEeqReview/IMPROVEeqReview.htm), 2006.
- Hand, J. L. and Malm, W. C.: Review of aerosol mass scattering efficiencies from ground-based measurements since 1990, *J. Geophys. Res. Atmos.*, 112(16), doi:10.1029/2007JD008484, 2007.
- 10 Haywood, J. M., Ramaswamy, V. and Soden, B. J.: Tropospheric Aerosol Climate Forcing in Clear-Sky Satellite Observations over the Oceans, *Science* (80-. ), 283(5406), 1999.
- IPCC 2007: Climate Change 2007: The Physical Science Basis (Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change), edited by: Solomon, S., Qin, D. Manning, M., Chen, Z., Marquis, M., Averyt, K. B., Tignor, M., and Miller, H. L., Cambridge Univ. Press, New York, USA, 131–217, 2007.
- 15 IPCC 2013: Climate Change 2013: The Physical Science Basis. Working Group I contribution to the IPCC fifth assessment report, Final Draft Underlying Scientific-Technical Assessment, Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 2013.
- Jacobson, M. Z.: Global direct radiative forcing due to multicomponent anthropogenic and natural aerosols, *J. Geophys. Res.*, 106(D2), 1551, doi:10.1029/2000JD900514, 2001a.
- 20 Jacobson, M. Z.: Strong radiative heating due to the mixing state of black carbon in atmospheric aerosols, *Nature*, 409(6821), 695–697, doi:10.1038/35055518, 2001b.
- Linke, C., Möhler, O., Veres, A., Mohácsi, Á., Bozóki, Z., Szabó, G. and Schnaiter, M.: Optical properties and mineralogical composition of different Saharan mineral dust samples: a laboratory study, *Atmos. Chem. Phys.*, 6(11), 3315–3323, doi:10.5194/acp-6-3315-2006, 2006.
- 25 Lu, Z., Streets, D. G., Winijkul, E., Yan, F., Chen, Y., Bond, T. C., Feng, Y., Dubey, M. K., Liu, S., Pinto, J. P. and Carmichael, G. R.: Light Absorption Properties and Radiative Effects of Primary Organic Aerosol Emissions, *Environ. Sci. Technol.*, 49(8), 4868–4877, doi:10.1021/acs.est.5b00211, 2015.
- Millán, M. M., Salvador, R., Mantilla, E. and Kallos, G.: Photooxidant dynamics in the Mediterranean basin in summer:

- Results from European research projects, *J. Geophys. Res.*, 102(D7), 8811, doi:10.1029/96JD03610, 1997.
- Minguillón, M. C., Ripoll, A., Pérez, N., Prévôt, A. S. H., Canonaco, F., Querol, X. and Alastuey, A.: Chemical characterization of submicron regional background aerosols in the western Mediterranean using an Aerosol Chemical Speciation Monitor, *Atmos. Chem. Phys.*, 15(11), 6379–6391, doi:10.5194/acp-15-6379-2015, 2015.
- 5 Moffet, R. C. and Prather, K. A.: In-situ measurements of the mixing state and optical properties of soot with implications for radiative forcing estimates., *Proc. Natl. Acad. Sci. U. S. A.*, 106(29), 11872–7, doi:10.1073/pnas.0900040106, 2009.
- Müller, T., Henzing, J. S., de Leeuw, G., Wiedensohler, A., Alastuey, A., Angelov, H., Bizjak, M., Collaud Coen, M., Engström, J. E., Gruening, C., Hillamo, R., Hoffer, A., Imre, K., Ivanow, P., Jennings, G., Sun, J. Y., Kalivitis, N., Karlsson, H., Komppula, M., Laj, P., Li, S.-M., Lunder, C., Marinoni, A., Martins dos Santos, S., Moerman, M., Nowak, A., Ogren, J.
- 10 A., Petzold, A., Pichon, J. M., Rodriguez, S., Sharma, S., Sheridan, P. J., Teinilä, K., Tuch, T., Viana, M., Virkkula, A., Weingartner, E., Wilhelm, R. and Wang, Y. Q.: Characterization and intercomparison of aerosol absorption photometers: result of two intercomparison workshops, *Atmos. Meas. Tech.*, 4(2), 245–268, doi:10.5194/amt-4-245-2011, 2011a.
- Müller, T., Laborde, M., Kassell, G. and Wiedensohler, A.: Design and performance of a three-wavelength LED-based total scatter and backscatter integrating nephelometer, *Atmos. Meas. Tech.*, 4(6), 1291–1303, doi:10.5194/amt-4-1291-2011,
- 15 2011b.
- Müller, T., Schladitz, a., Kandler, K. and Wiedensohler, a.: Spectral particle absorption coefficients, single scattering albedos and imaginary parts of refractive indices from ground based in situ measurements at Cape Verde Island during SAMUM-2, *Tellus, Ser. B Chem. Phys. Meteorol.*, 63, 573–588, doi:10.1111/j.1600-0889.2011.00572.x, 2011c.
- Obiso, V., Pandolfi, M., Ealo, M. and Jorba, O.: Impact of aerosol microphysical properties on mass scattering cross
- 20 sections, *J. Aerosol Sci.*, 112, doi:10.1016/j.jaerosci.2017.03.001, 2017.
- de P. Vasconcelos, L. A., Macias, E. S., McMurry, P. H., Turpin, B. J. and White, W. H.: A closure study of extinction apportionment by multiple regression, *Atmos. Environ.*, 35(1), 151–158, doi:10.1016/S1352-2310(00)00273-9, 2001.
- Paatero, P.: Least squares formulation of robust non-negative factor analysis, *Chemometr. Intell. Lab.*, 37, 23–35, 1997.
- Paatero, P.: User's guide for positive matrix factorization programs PMF2 and PMF3, Part 1: tutorial, University of Helsinki,
- 25 Helsinki, Finland, 2004.
- Paatero, P. and Hopke, P. K.: Discarding or downweighting high noise variables in factor analytic models, *Anal. Chim. Ac.*, 490, 277–289, doi:10.1016/s0003-2670(02)01643-4, 2003.

- Paatero, P., Hopke, P. K., Begum, B. A., and Biswas, S. K.: A graphical diagnostic method for assessing the rotation in factor analytical models of atmospheric pollution, *Atmos. Environ.*, 39, 193–201, doi:10.1016/j.atmosenv.2004.08.018, 2005.
- Paatero, P., Hopke, P. K., Song, X., and Ramadan, Z.: Understanding and controlling rotations in factor analytic models, *Chemometr. Intell. Lab.*, 60, 253–264, 2002.
- Paatero, P. and Tapper, U.: Positive Matrix Factorization: a non negative factor model with optimal utilization of error estimates of data values, *Environmetrics*, 5, 111–126, 1994.
- Pandolfi, M., Cusack, M., Alastuey, a. and Querol, X.: Variability of aerosol optical properties in the Western Mediterranean Basin, *Atmos. Chem. Phys.*, 11(15), 8189–8203, doi:10.5194/acp-11-8189-2011, 2011.
- 10 Pandolfi, M., Ripoll, A., Querol, X. and Alastuey, A.: Climatology of aerosol optical properties and black carbon mass absorption cross section at a remote high-altitude site in the western Mediterranean Basin, *Atmos. Chem. Phys.*, 14(12), 6443–6460, doi:10.5194/acp-14-6443-2014, 2014a.
- Pandolfi, M., Querol, X., Alastuey, A., Jimenez, J. L., Jorba, O., Day, D., Ortega, A., Cubison, M. J., Comerón, A., Sicard, M., Mohr, C., Prévôt, A. S. H., Minguillón, M. C., Pey, J., Baldasano, J. M., Burkhardt, J. F., Seco, R., Peñuelas, J., van Drooge, B. L., Artiñano, B., Di Marco, C., Nemitz, E., Schallhart, S., Metzger, A., Hansel, A., Lorente, J., Ng, S., Jayne, J. and Szidat, S.: Effects of sources and meteorology on particulate matter in the Western Mediterranean Basin: An overview of the DAURE campaign, *J. Geophys. Res. Atmos.*, 119(8), 4978–5010, doi:10.1002/2013JD021079, 2014b.
- 15 Pandolfi, M., Alastuey, A., Pérez, N., Reche, C., Castro, I., Shatalov, V. and Querol, X.: Trends analysis of PM source contributions and chemical tracers in NE Spain during 2004–2014: a multi-exponential approach, *Atmos. Chem. Phys.*, 16(18), 11787–11805, doi:10.5194/acp-16-11787-2016, 2016.
- 20 Pereira, S., Wagner, F. and Silva, A. M.: Scattering properties and mass concentration of local and long-range transported aerosols over the South Western Iberia Peninsula, *Atmos. Environ.*, 42(33), 7623–7631, doi:10.1016/j.atmosenv.2008.06.008, 2008.
- Pérez, C., Sicard, M., Jorba, O., Comerón, A. and Baldasano, J. M.: Summertime re-circulations of air pollutants over the north-eastern Iberian coast observed from systematic EARLINET lidar measurements in Barcelona, *Atmos. Environ.*, 38, 3983–4000, doi:10.1016/j.atmosenv.2004.04.010, 2004.
- 25 Pérez, N., Pey, J., Castillo, S., Viana, M., Alastuey, A. and Querol, X.: Interpretation of the variability of levels of regional background aerosols in the Western Mediterranean, *Sci. Total Environ.*, 407(1), 527–540, doi:10.1016/j.scitotenv.2008.09.006, 2008a.

- Pérez, N., Pey, J., Querol, X., Alastuey, A., López, J. M. and Viana, M.: Partitioning of major and trace components in PM<sub>10</sub>–PM<sub>2.5</sub>–PM<sub>1</sub> at an urban site in Southern Europe, *Atmos. Environ.*, 42(8), 1677–1691, doi:10.1016/j.atmosenv.2007.11.034, 2008b.
- 5   Pey, J., Rodríguez, S., Querol, X., Alastuey, A., Moreno, T., Putaud, J. P. and Van Dingenen, R.: Variations of urban aerosols in the western Mediterranean, *Atmos. Environ.*, 42(40), 9052–9062, doi:10.1016/j.atmosenv.2008.09.049, 2008.
- Pey, J., Pérez, N., Castillo, S., Viana, M., Moreno, T., Pandolfi, M., López-Sebastián, J. M., Alastuey, A. and Querol, X.: Geochemistry of regional background aerosols in the Western Mediterranean, *Atmos. Res.*, 94(3), 422–435, doi:10.1016/j.atmosres.2009.07.001, 2009.
- 10   Pey, J., Pérez, N., Querol, X., Alastuey, A., Cusack, M. and Reche, C.: Intense winter atmospheric pollution episodes affecting the Western Mediterranean., *Sci. Total Environ.*, 408(8), 1951–9, doi:10.1016/j.scitotenv.2010.01.052, 2010.
- Pey, J., Pérez, N., Cortés, J., Alastuey, A. and Querol, X.: Chemical fingerprint and impact of shipping emissions over a western Mediterranean metropolis: Primary and aged contributions, *Sci. Total Environ.*, 463, 497–507, doi:10.1016/j.scitotenv.2013.06.061, 2013.
- 15   Pitchford, M., Maim, W., Schichtel, B., Kumar, N., Lowenthal, D. and Hand, J.: Revised algorithm for estimating light extinction from IMPROVE particle speciation data., *J. Air Waste Manag. Assoc.*, 57(11), 1326–36, 2007.
- Querol, X., Alastuey, A., Pandolfi, M., Reche, C., Pérez, N., Minguillón, M. C., Moreno, T., Viana, M., Escudero, M., Orio, A., Pallarés, M. and Reina, F.: 2001-2012 trends on air quality in Spain., *Sci. Total Environ.*, 490, 957–69, doi:10.1016/j.scitotenv.2014.05.074, 2014.
- 20   Querol, X., Alastuey, A., Rodriguez, S., Plana, F., Mantilla, E. and Ruiz, C. R.: Monitoring of PM<sub>10</sub> and PM<sub>2.5</sub> around primary particulate anthropogenic emission sources, *Atmos. Environ.*, 35(5), 845–858, doi:10.1016/S1352-2310(00)00387-3, 2001.
- Querol, X., Pey, J., Pandolfi, M., Alastuey, a., Cusack, M., Pérez, N., Moreno, T., Viana, M., Mihalopoulos, N., Kallos, G. and Kleanthous, S.: African dust contributions to mean ambient PM<sub>10</sub> mass-levels across the Mediterranean Basin, *Atmos. Environ.*, 43, 4266–4277, doi:10.1016/j.atmosenv.2009.06.013, 2009.
- 25   Ramana, M. V., Ramanathan, V., Feng, Y., Yoon, S.-C., Kim, S.-W., Carmichael, G. R. and Schauer, J. J.: Warming influenced by the ratio of black carbon to sulphate and the black-carbon source, *Nat. Geosci.*, 3(8), 542–545, doi:10.1038/ngeo918, 2010.
- Ramanathan, V. and Carmichael, G.: Global and regional climate changes due to black carbon, *Nat. Geosci.*, 1(4), 221–227,

doi:10.1038/ngeo156, 2008.

- Reche, C., Querol, X., Alastuey, A., Viana, M., Pey, J., Moreno, T., Rodríguez, S., González, Y., Fernández-Camacho, R., de la Rosa, J., Dall'Osto, M., Prévôt, A. S. H., Hueglin, C., Harrison, R. M. and Quincey, P.: New considerations for PM, Black Carbon and particle number concentration for air quality monitoring across different European cities, *Atmos. Chem. Phys.*, 11(13), 6207–6227, doi:10.5194/acp-11-6207-2011, 2011.
- Ripoll, A., Minguillón, M. C., Pey, J., Pérez, N., Querol, X. and Alastuey, A.: Joint analysis of continental and regional background environments in the western Mediterranean: PM<sub>1</sub> and PM<sub>10</sub> concentrations and composition, *Atmos. Chem. Phys.*, 15(2), 1129–1145, doi:10.5194/acp-15-1129-2015, 2015a.
- Ripoll, A., Minguillón, M. C., Pey, J., Jimenez, J. L., Day, D. A., Sosedova, Y., Canonaco, F., Prévôt, A. S. H., Querol, X. and Alastuey, A.: Long-term real-time chemical characterization of submicron aerosols at Montsec (southern Pyrenees, 1570 m a.s.l.), *Atmos. Chem. Phys.*, 15(6), 2935–2951, doi:10.5194/acp-15-2935-2015, 2015b.
- Ripoll, A., Pey, J., Minguillón, M. C., Pérez, N., Pandolfi, M., Querol, X. and Alastuey, A.: Three years of aerosol mass, black carbon and particle number concentrations at Montsec (southern Pyrenees, 1570 m a.s.l.), *Atmos. Chem. Phys.*, 14, 4279–4295, doi:10.5194/acp-14-4279-2014, 2014.
- Rodríguez, S., Querol, X., Alastuey, A. and Plana, F.: Sources and processes affecting levels and composition of atmospheric aerosol in the western Mediterranean, *J. Geophys. Res.*, 107(D24), 4777, doi:10.1029/2001JD001488, 2002.
- Ryan, P. A., Lowenthal, D. and Kumar, N.: Improved light extinction reconstruction in interagency monitoring of protected visual environments., *J. Air Waste Manag. Assoc.*, 55(11), 1751–9, 2005.
- Saxe, H. and Larsen, T.: Air pollution from ships in three Danish ports, *Atmos. Environ.*, 38(24), 4057–4067, doi:10.1016/j.atmosenv.2004.03.055, 2004.
- Schembari, C., Cavalli, F., Cuccia, E., Hjorth, J., Calzolari, G., Pérez, N., Pey, J., Prati, P., Raes, F. Impact of a European directive on ship emissions on air quality in Mediterranean harbours. *Atmospheric Environment* 61, 661-669, 2012.
- Schuster, G. L., Dubovik, O. and Holben, B. N.: Angstrom exponent and bimodal aerosol size distributions, *J. Geophys. Res.*, 111(D7), D07207, doi:10.1029/2005JD006328, 2006.
- Shindell, D., Kuylensstierna, J. C. I., Vignati, E., van Dingenen, R., Amann, M., Klimont, Z., Anenberg, S. C., Muller, N., Janssens-Maenhout, G., Raes, F., Schwartz, J., Faluvegi, G., Pozzoli, L., Kupiainen, K., Höglund-Isaksson, L., Emberson, L., Streets, D., Ramanathan, V., Hicks, K., Oanh, N. T. K., Milly, G., Williams, M., Demkine, V. and Fowler, D.: Simultaneously Mitigating Near-Term Climate Change and Improving Human Health and Food Security, *Science* (80-. ),

335(6065), 2012.

Sun, Y., Wang, Z., Wild, O., Xu, W., Chen, C., Fu, P., Du, W., Zhou, L., Zhang, Q., Han, T., Wang, Q., Pan, X., Zheng, H., Li, J., Guo, X., Liu, J. and Worsnop, D. R.: “APEC Blue”: Secondary Aerosol Reductions from Emission Controls in Beijing, *Sci. Rep.*, 6(1), 20668, doi:10.1038/srep20668, 2016.

- 5 Turpin, B. J., Saxena, P. and Andrews, E.: Measuring and simulating particulate organics in the atmosphere: problems and prospects, *Atmos. Environ.*, 34(18), 2983–3013, doi:10.1016/S1352-2310(99)00501-4, 2000.

Updyke, K. M., Nguyen, T. B. and Nizkorodov, S. A.: Formation of brown carbon via reactions of ammonia with secondary organic aerosols from biogenic and anthropogenic precursors, *Atmos. Environ.*, 63, 22–31, doi:10.1016/j.atmosenv.2012.09.012, 2012.

- 10 Viana, M., Kuhlbusch, T. A. J., Querol, X., Alastuey, A., Harrison, R. M., Hopke, P. K., Winiwarter, W., Vallius, M., Szidat, S., Prévôt, A. S. H., Hueglin, C., Bloemen, H., Wählin, P., Vecchi, R., Miranda, A. I., Kasper-Giebl, A., Maenhaut, W. and Hitzenberger, R.: Source apportionment of particulate matter in Europe: A review of methods and results, *J. Aerosol Sci.*, 39(10), 827–849, doi:10.1016/j.jaerosci.2008.05.007, 2008.

- Viana, M., Amato, F., Alastuey, A., Querol, X., Moreno, T., García Dos Santos, S., Herce, M. D. and Fernández-Patier, R.: Chemical Tracers of Particulate Emissions from Commercial Shipping, *Environ. Sci. Technol.*, 43(19), 7472–7477, doi:10.1021/es901558t, 2009.

Viana, M., Hammingh, P., Colette, A., Querol, X., Degraeuwe, B., Vlieger, I. de and van Aardenne, J.: Impact of maritime transport emissions on coastal air quality in Europe, *Atmos. Environ.*, 90, 96–105, doi:10.1016/j.atmosenv.2014.03.046, 2014.

- 20 Vrekoussis, M., Liakakou, E., Koçak, M., Kubilay, N., Oikonomou, K., Sciare, J. and Mihalopoulos, N.: Seasonal variability of optical properties of aerosols in the Eastern Mediterranean, *Atmos. Environ.*, 39(37), 7083–7094, doi:10.1016/j.atmosenv.2005.08.011, 2005.

- Wagner, F., Bortoli, D., Pereira, S., Costa, M. J., Silva, A. M., Weinzierl, B., Esselborn, M., Petzold, A., Rasp, K., Heinold, B. and Tegen, I.: Properties of dust aerosol particles transported to Portugal from the Sahara desert, *Tellus B*, 61(1), doi:10.3402/tellusb.v61i1.16830, 2009.

White, W. H., and E. S. Macias (1987), On measurement error and the empirical relationship of atmospheric extinction to aerosol composition in the non-urban West, in *Visibility Protection: Research and Policy Aspects*, edited by. P. S. Bhardwaja, pp. 783–744, Air Pollut. Control Assoc., Pittsburgh, Pa.

WMO/GAW report 227: Aerosol Measurement Procedures, Guidelines and Recommendations, 2nd Edition, 2016, 103 pp.  
August 2016 (WMO-No. 1177).

Zanatta, M., Cavalli, F., Gysel, M., Weingartner, E., Bukowiecki, N., Putaud, J. P., Müller, T., Baltensperger, U. and Laj, P.:  
A European aerosol phenomenology -5: climatology of black carbon optical properties at 9 regional background sites across  
5 Europe, EGU Gen. Assem. 2016, held 17-22 April. 2016 Vienna Austria, p.15335, 18, 15335, 2016.

10

15

20

## Figure captions

**Figure 1.** Map location and topographic profiles of Barcelona (BCN; urban background), Montseny (MSY; regional background) and Montsec (MSA; remote mountain-top background) measurement sites.

5

**Figure 2.** (a) Source chemical profiles and (b) source contributions to  $\text{PM}_{10}$  mass concentration obtained at MSA by means of the PMF model.  $\text{PM}_{10}$  average concentration, and absolute ( $\mu\text{g m}^{-3}$ ) and relative (%) source contributions are reported for the study period (2010-2014).

10 | **Figure 3.** Relative (%) monthly average source contribution to:  $\text{PM}_{10}$  concentration ( $\mu\text{g m}^{-3}$ ) (a, b and c [at BCN, MSY and MSA, respectively](#)), absorption ( $\text{Mm}^{-1}$ ) at 637 nm (d, e and f) and scattering ( $\text{Mm}^{-1}$ ) at 525 nm (g and h).  $\text{PM}_{10}$  source contributions were obtained from the PMF model, whereas scattering and absorption contributions ~~have been~~[were](#) modelled by means of the PMF-MLR technique. The study period ranges between 2004-2014 at BCN and MSY and between 2010-2014 at MSA.

15

**Figure 4.** Relationship between measured and modeled optical parameters: absorption at 637 nm (a, b, and c for MSA, MSY and BCN respectively) ~~and~~[and](#), scattering at 525nm (d and e for MSA and MSY) ~~and SSA at MSY (f)~~.

20

**Figure 5.** Average fractional bias (FB) calculated for the [observed](#)-modeled ~~data pairs of and measured~~ scattering ( $S_c$ ) and absorption (Abs) coefficients at BCN, MSY and MSA broken down by quintile from the lowest to highest scattering and absorption coefficient values. “n” accounts for the number of daily data points used in the FB calculation.

25

**Figure 6.** [Relationship between measured and modeled \(a\) scattering at 525 nm and \(b\) absorption at 637 nm at MSY for the period January 2015-December 2015.](#)

**Figure 7.** Time series of the daily average modeled and measured extensive optical coefficients (scattering at 525 nm and absorption at 637 nm) for (a) BCN and (b) MSY during the period 2004-2014, and for (c) MSA during the period 2010-2014.

30

~~**Figure 7.** Boxplots time series of the modeled (white box) and measured (grey box) annual average of SSA at MSY during the period 2004-2014.~~



**Figure 8.** Temporal trends ~~for~~ the monthly average ~~of~~ absorption at 637 nm ~~and~~ scattering at 525 nm ~~and SSA series~~ obtained by means of the multi-exponential test at MSY during the period 2004-2014. The time series were decomposed in: simulated coefficient (green), trend (red), main component (black), seasonal component (blue) and residue (grey).

5

**Table 1.** Absolute ( $\mu\text{g m}^{-3}$ ) and relative (%) average source contribution to  $\text{PM}_{10}$  at BCN and MSY during the period 2004-2014 (Pandolfi et al., 2016), and for MSA during the period 2010-2014.

( $\mu\text{g m}^{-3}$ ; %)	$\text{PM}_{10}$	Aged marine	Mineral	Aged organics	<del>Amm-Secondary</del> nitrate	<del>Amm-Secondary</del> sulfate	Industrial/ Traffic	Industrial/ Metallurgy	V-Ni	Traffic	Road <del>dust</del> resuspension
BCN	34.0; 100	5.73; 16.9	4.61; 13.6		4.45; 13.1	4.67; 13.7		0.96; 2.8	3.32; 9.8	5.14; 15.1	4.25; 12.5
MSY	16.7; 100	1.76; 10.6	2.70; 16.2	3.78; 22.7	1.31; 7.9	3.95; 23.7	1.43; 8.6		0.71; 4.3		
MSA	9.65; 100	1.08; 11.1	2.27; 23.6	2.84; 29.4	0.72; 7.5	0.87; 9.0	1.09; 11.3		0.79; 8.2		

15

20

**Table 2.** Scattering and absorption efficiencies (MSE and MAE;  $\text{m}^2 \text{g}^{-1}$ ) calculated for the different aerosol sources identified by PMF at BCN, MSY and MSA in the  $\text{PM}_{10}$  fraction. Scattering Ångström exponent (SAE) and single scattering albedo (SSA) coefficients were obtained for each source at MSY and MSA. Note that SAE was not considered for the *Aged marine* source at Montsec due to the  $\text{PM}_{2.5}$  cut-off inlet. The study period ranges between 2010-2014 at BCN and MSY and 2011-2014 at MSA.

\*SAE for the *Industrial/Traffic* source at MSY was calculated in the range 450-525 nm.

		Aged marine	Mineral	Aged organics	SecondaryAmmoniumnitrate	SecondaryAmmoniumsulfate	Industrial/Traffic	Industrial/Metallurgy	V-Ni	Traffic	Road dust resuspension
BCN	MAE 637	0.108 ± 0.021	0.087 ± 0.050		0.284 ± 0.040	0.359 ± 0.035		0.138 ± 0.185	0.928 ± 0.058	1.672 ± 0.050	0.062 ±0.084
MSY	MSE 450	1.205 ± 0.385	1.046 ± 0.130	1.990 ± 0.258	10.456 ± 0.494	5.860 ± 0.256	2.241 ± 0.982		10.844 ± 1.850		
	MSE 525	1.211 ± 0.316	1.262 ± 0.106	1.414 ± 0.212	8.783 ± 0.405	4.508 ± 0.210	2.057 ± 0.805		8.029 ± 1.516		
	MSE 635	1.201 ± 0.284	1.429 ± 0.096	0.916 ± 0.190	6.980 ± 0.364	3.092 ± 0.188	2.425 ± 0.723		4.687 ± 1.362		
	MAE 637	0.027 ± 0.018	0.005 ± 0.007	0.169 ± 0.011	0.234 ± 0.028	0.122 ± 0.010	0.867 ± 0.047		0.526 ± 0.065		
	SAE	0.010	-0.896	2.254	1.175	1.861	0.556*		2.451		
	SSA	0.978	0.997	0.844	0.968	0.962	0.736		0.899		
MSA	MSE 450	0.036 ± 0.407	0.931 ± 0.115	2.114 ± 0.338	9.839 ± 0.978	13.825 ± 0.792	2.714 ± 0.644		4.823 ± 0.659		
	MSE 525	(-)0.054 ± 0.332	1.077 ± 0.093	1.335 ± 0.275	7.839 ± 0.797	10.699 ± 0.537	2.354 ± 0.525		3.538 ± 0.537		
	MSE 635	(-)0.036 ± 0.268	1.276 ± 0.076	0.617 ± 0.223	6.006 ± 0.645	7.439 ± 0.522	2.044 ± 0.425		2.274 ± 0.435		
	MAE 637	0.015 ± 0.010	0.029 ± 0.003	0.14 ± 0.009	0.364 ± 0.023	0.173 ± 0.021	0.206 ± 0.016		0.165 ± 0.017		
	SAE	-	-0.914	3.594	1.432	1.804	0.819		2.189		

10

15

20

**Table 3.** Theil-Sen (TS) trends at a 95% confidence level for deseasonalized monthly averages ~~time series~~ of scattering ~~and~~ absorption ~~and single scattering albedo (SSA) time series coefficients~~ at MSY during the period 2004-2014. AR (Mm<sup>-1</sup>; %)= Average reduction; TR (%)= Total reduction; The significance of the trends (p-value trend) was obtained by means of TS method using monthly averages: \*\*\* (p-value < 0.001), \*\* (p-value < 0.01), \* (p-value <0.05). The Non-linearity parameter (%) was calculated by means of the multi-exponential (ME) test.

		TS				ME
		p-value slope	AR (Mm <sup>-1</sup> yr <sup>-1</sup> )	AR (% yr <sup>-1</sup> )	TR (%)	NL (%)
MSY	Sc 525	***	-2.14	-4.57	-50 <del>2</del>	5.56
	Abs 637	***	-0.16	-4.13	-45 <del>4</del>	4.17
	<del>SSA</del>	<del>***</del>	<del>-0.001</del>	<del>-0.11</del>	<del>-1.24</del>	<del>0.002</del>

		TS				ME
		<u>p-value slope</u>	<u>AR (Mm<sup>-1</sup> yr<sup>-1</sup>)</u>	<u>AR (% yr<sup>-1</sup>)</u>	<u>TR (%)</u>	<u>NL (%)</u>
<u>MSY</u>	<u>Sc 525</u>	<u>***</u>	<u>-2.14</u>	<u>-4.57</u>	<u>-50</u>	<u>5.56</u>
	<u>Abs 637</u>	<u>***</u>	<u>-0.16</u>	<u>-4.13</u>	<u>-45</u>	<u>4.17</u>

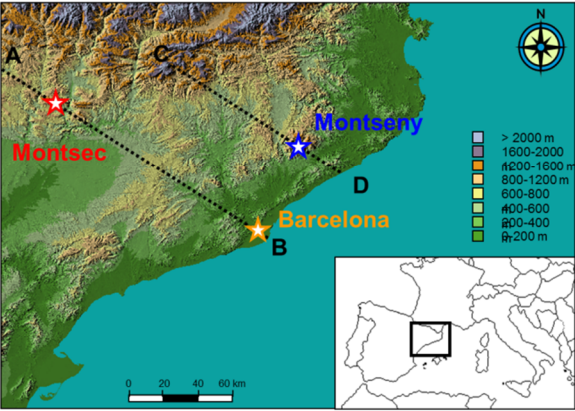
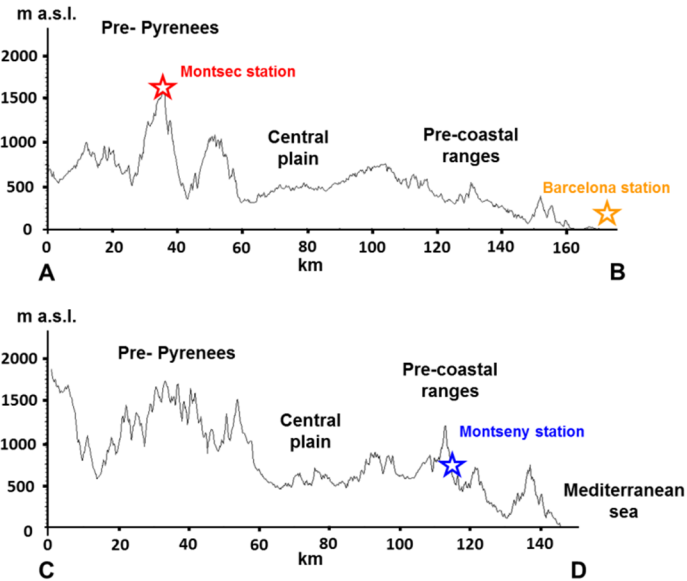
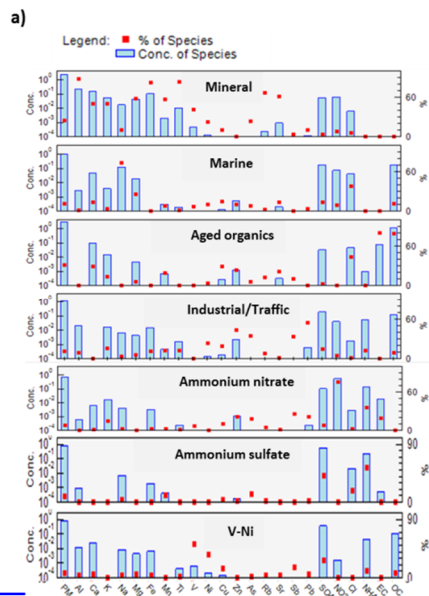


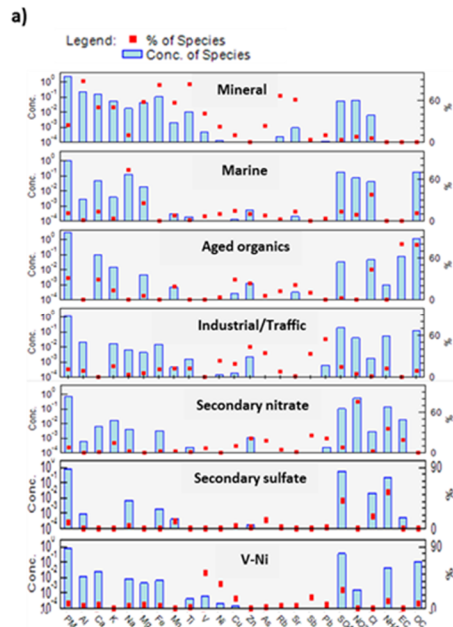
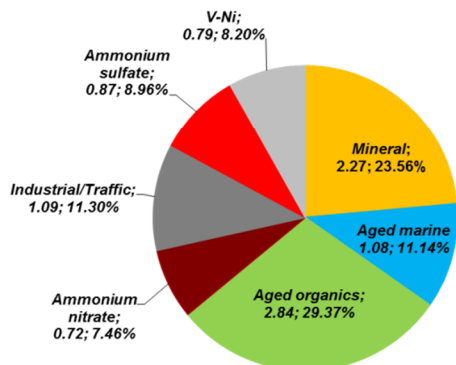
Figure 1





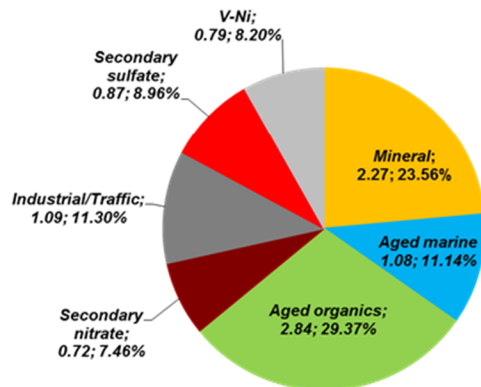
b)

MSA  
 $\langle PM_{10} \rangle = 9.65 \mu g/m^3$



b)

MSA  
 $\langle PM_{10} \rangle = 9.65 \mu g/m^3$



5 Figure 2

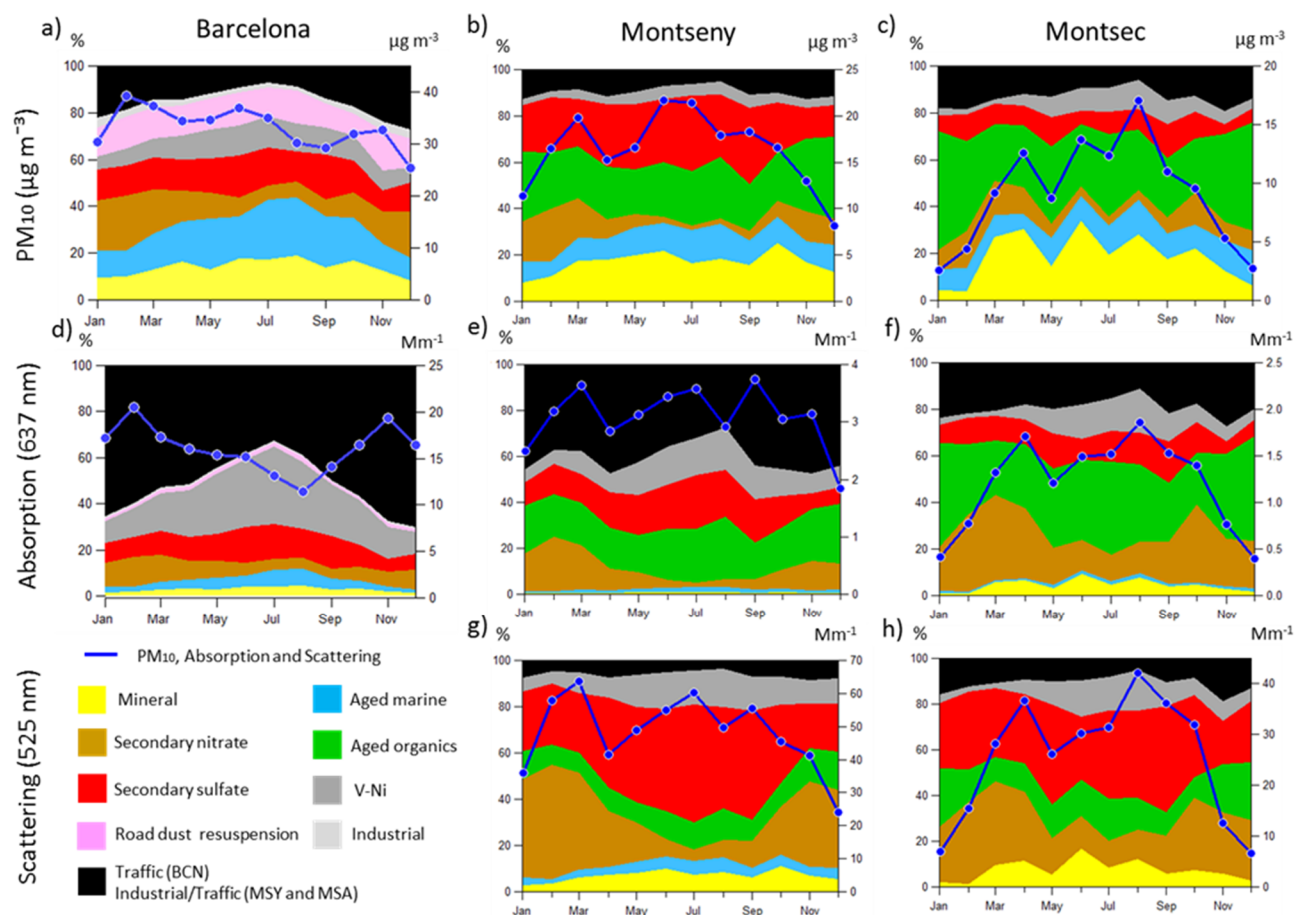


Figure 3

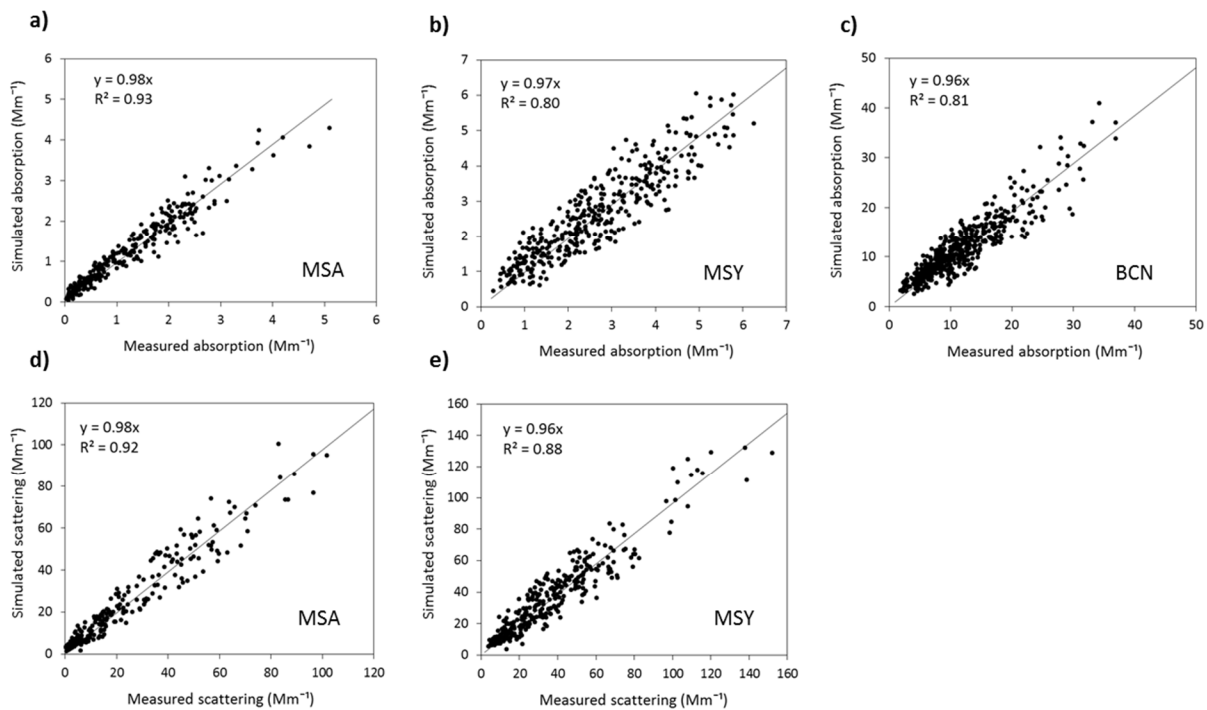
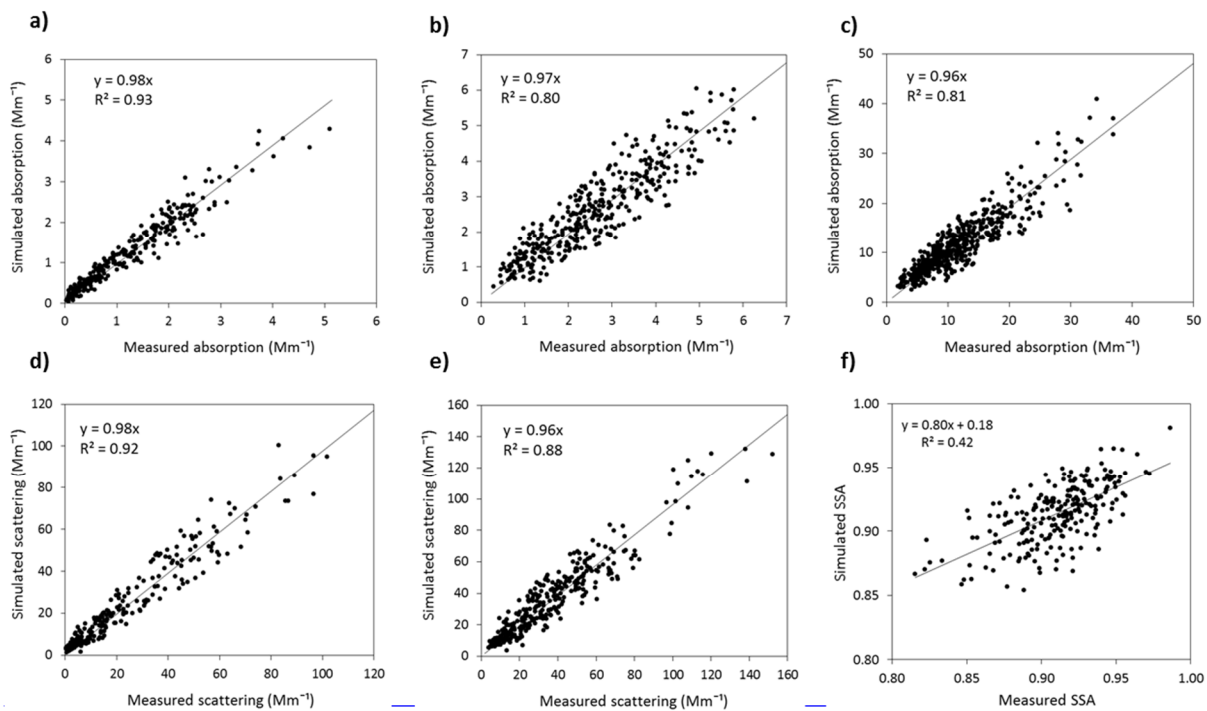
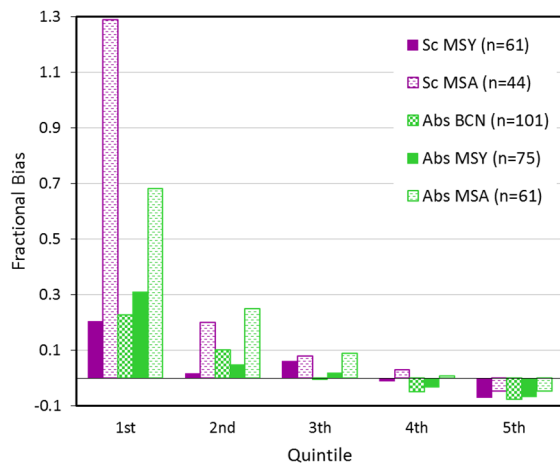


Figure 4

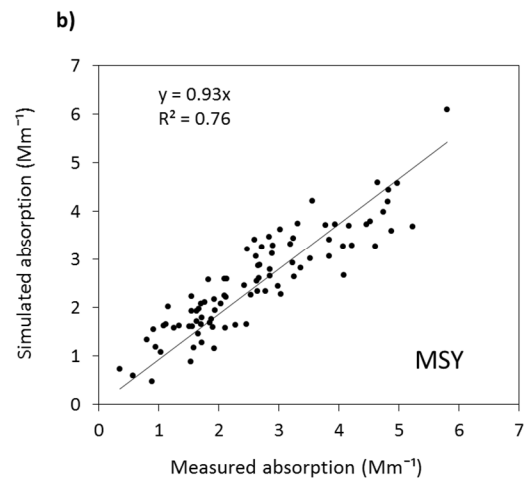
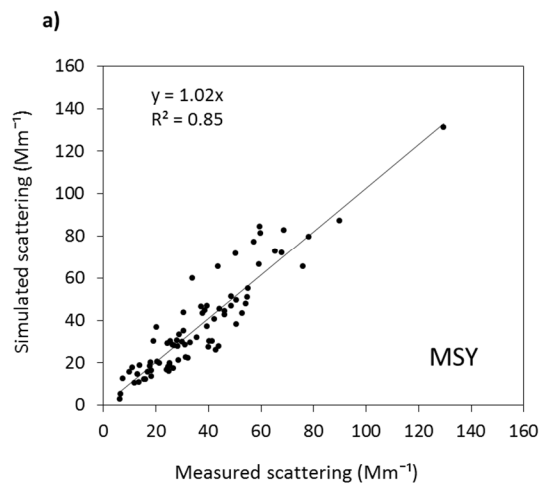


**Figure 5**

5

10





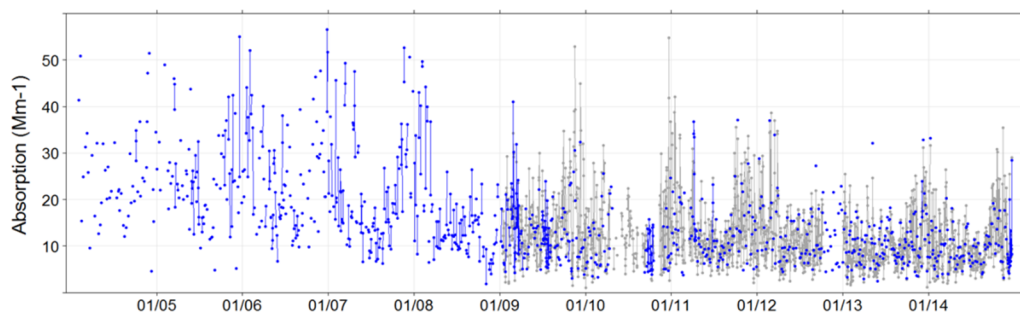
**Figure 6**

5

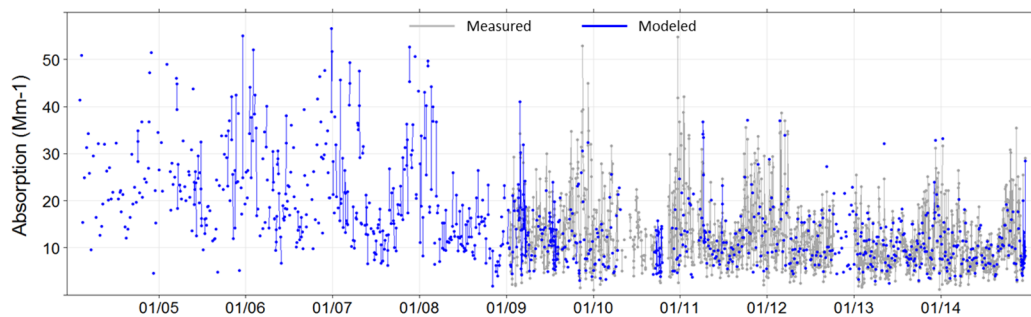
10

15

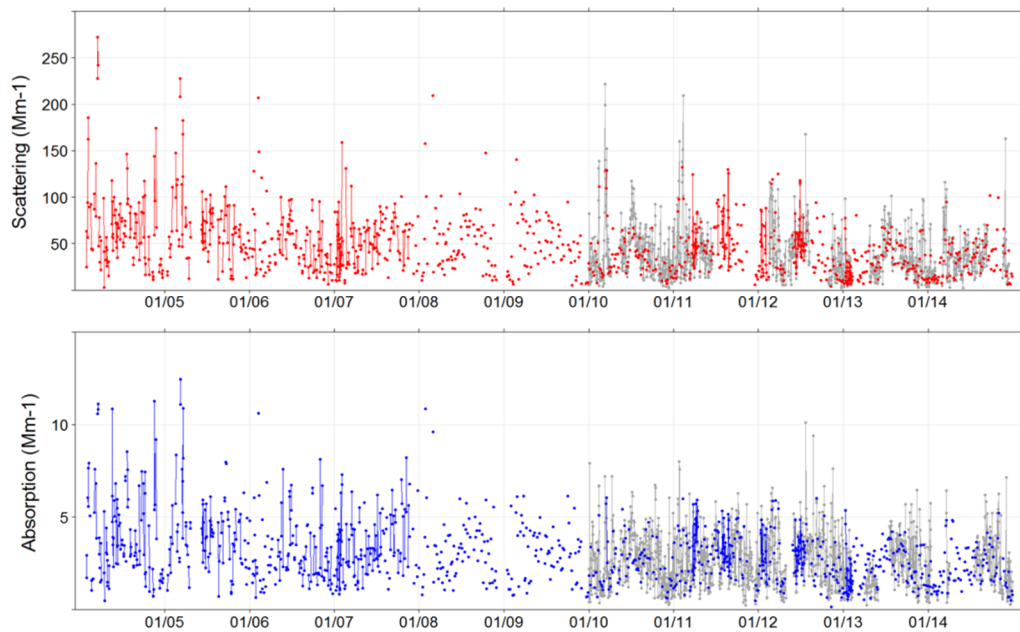
a)



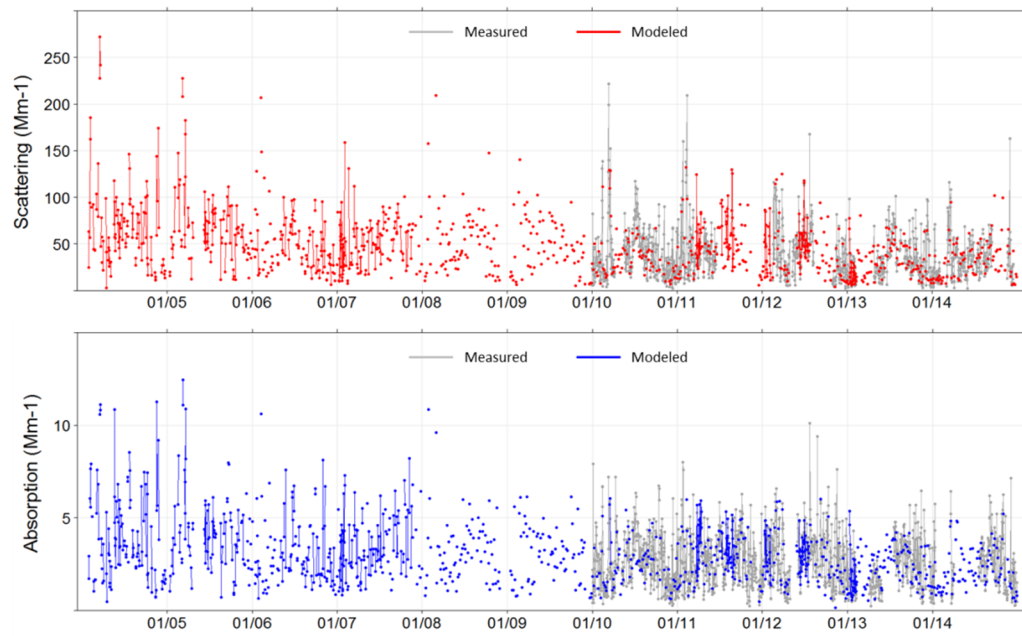
a) BCN



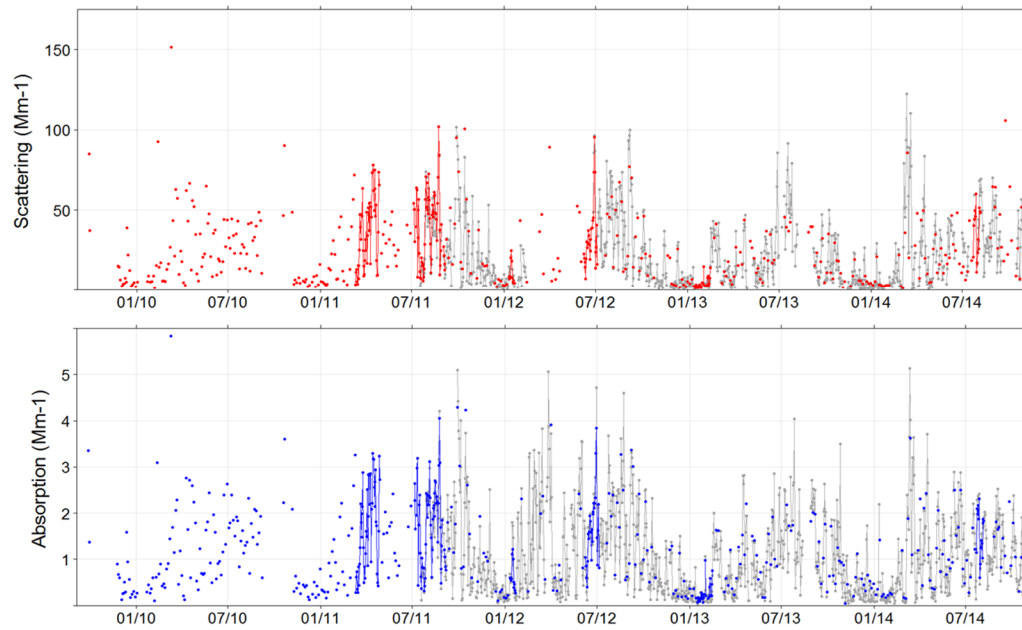
b)



b) MSY



c)



c) MSA

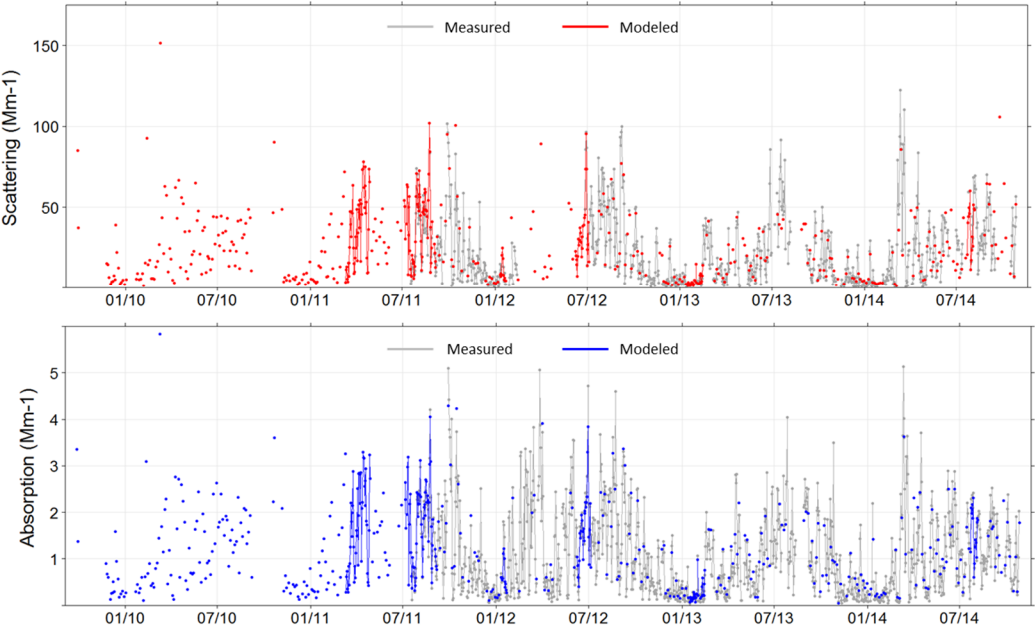


Figure 76

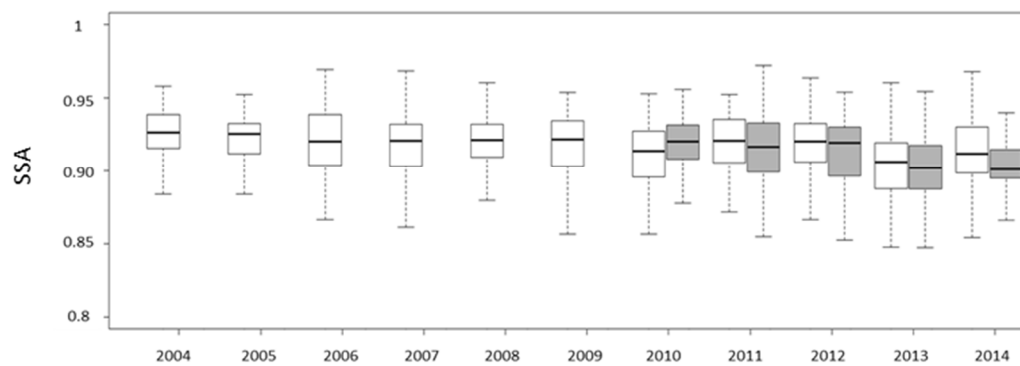


Figure 7

5

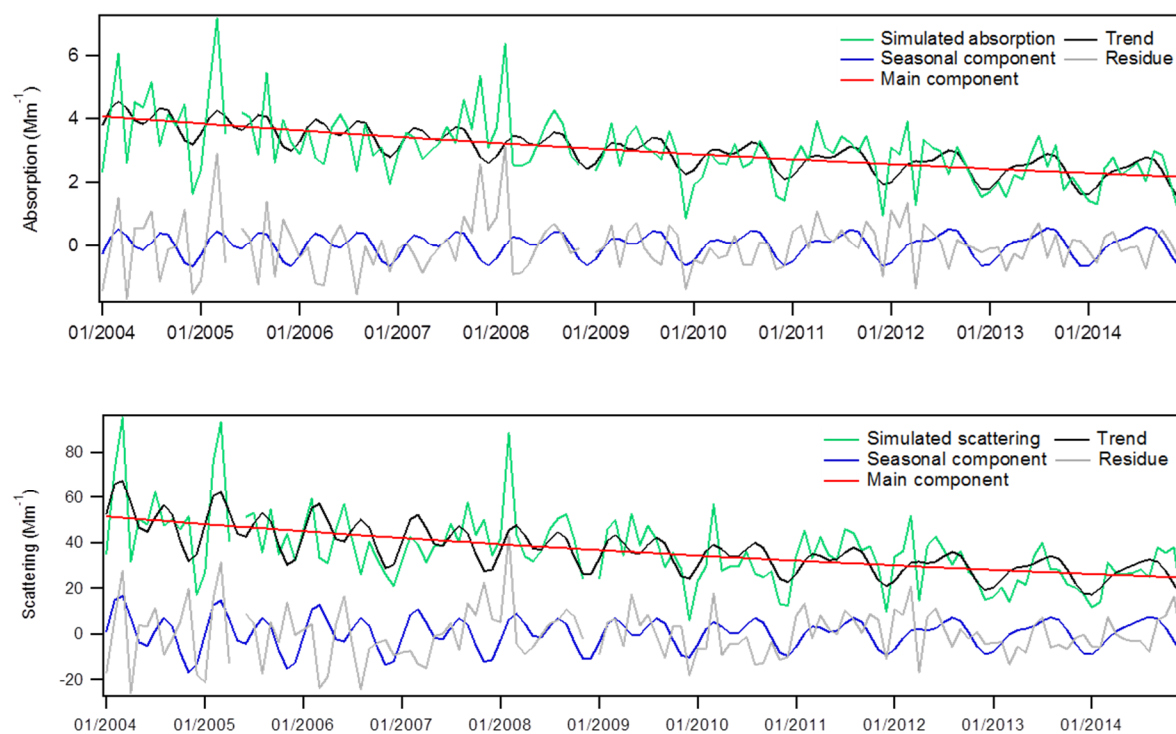


Figure 8

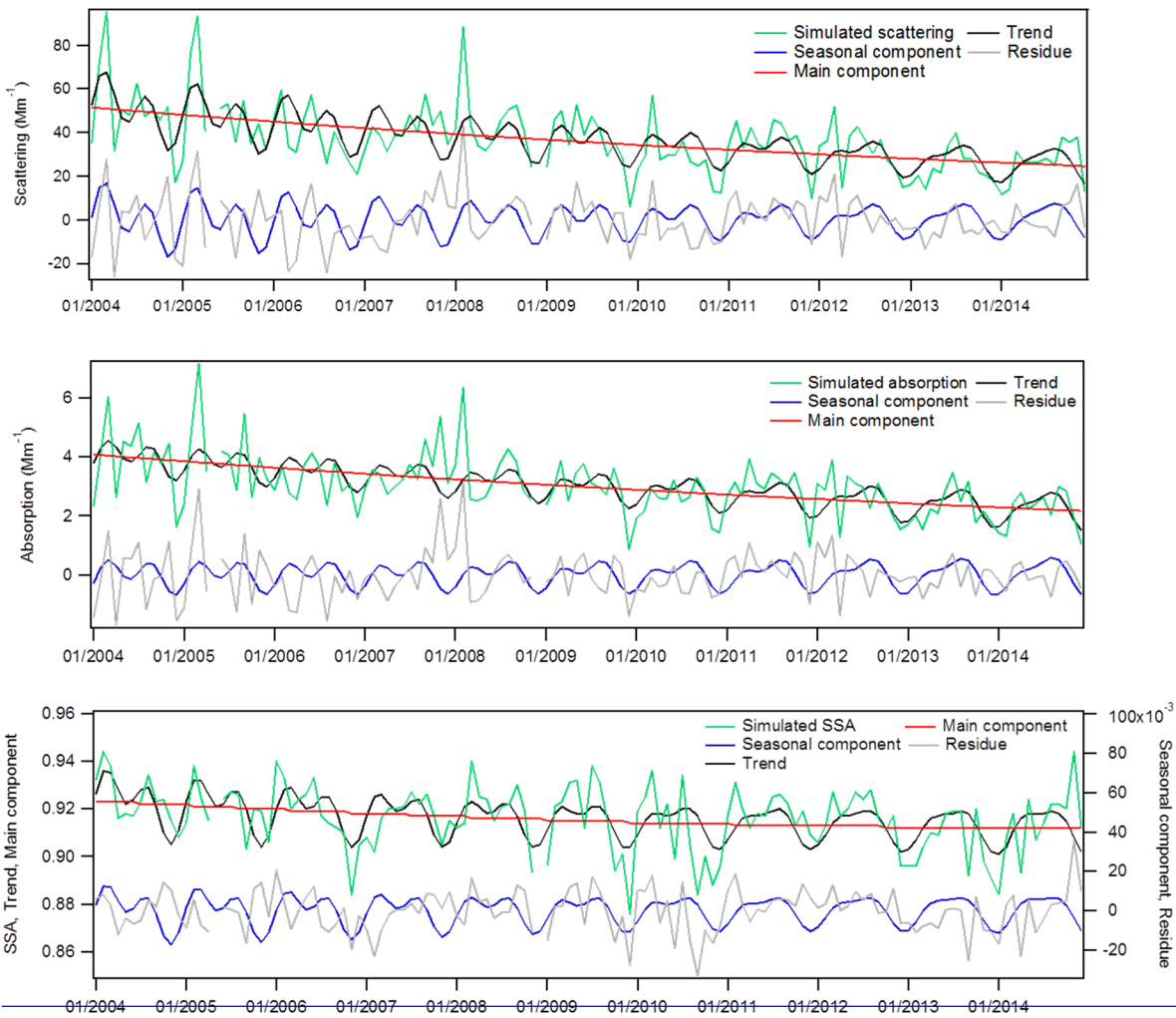
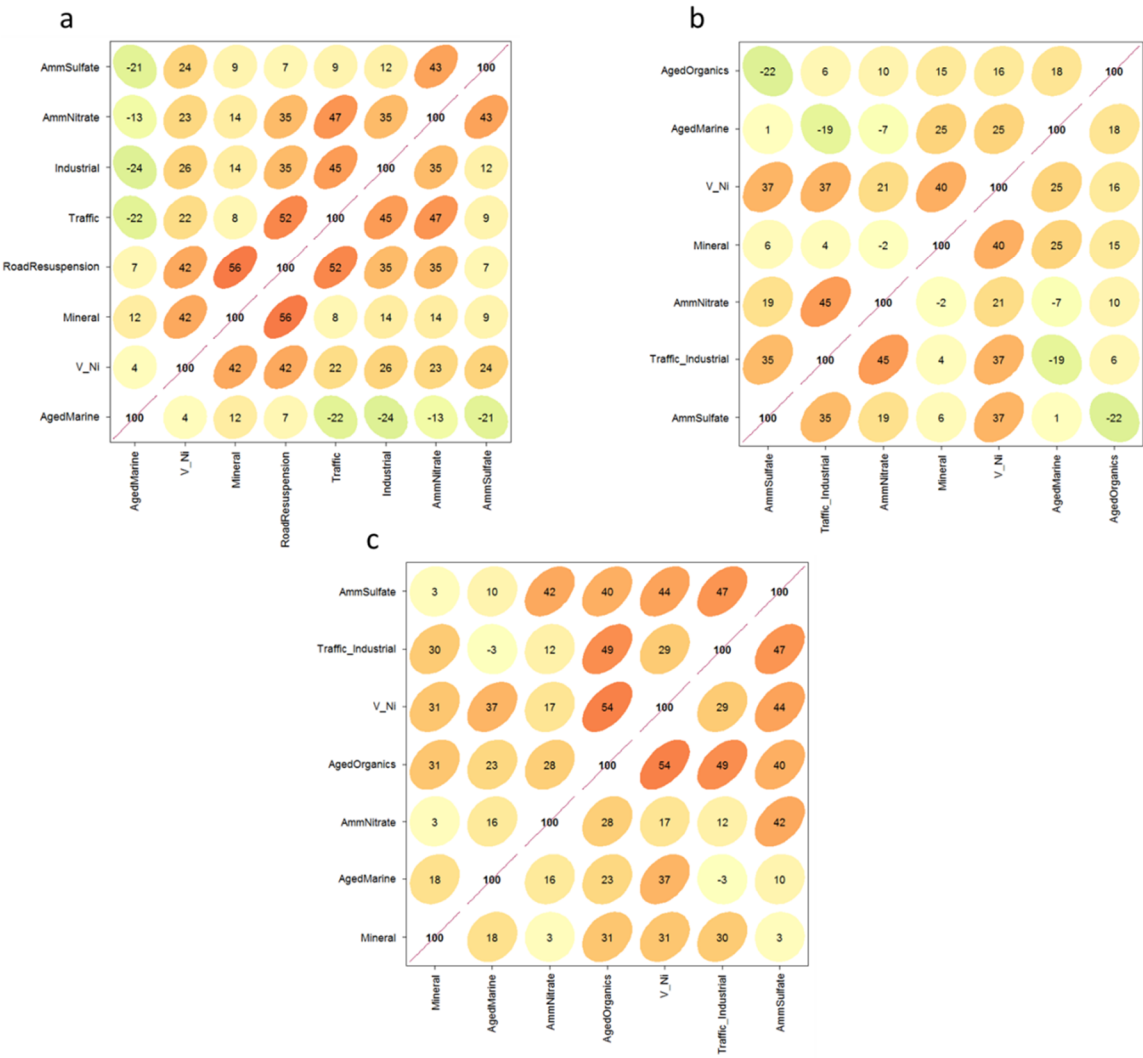
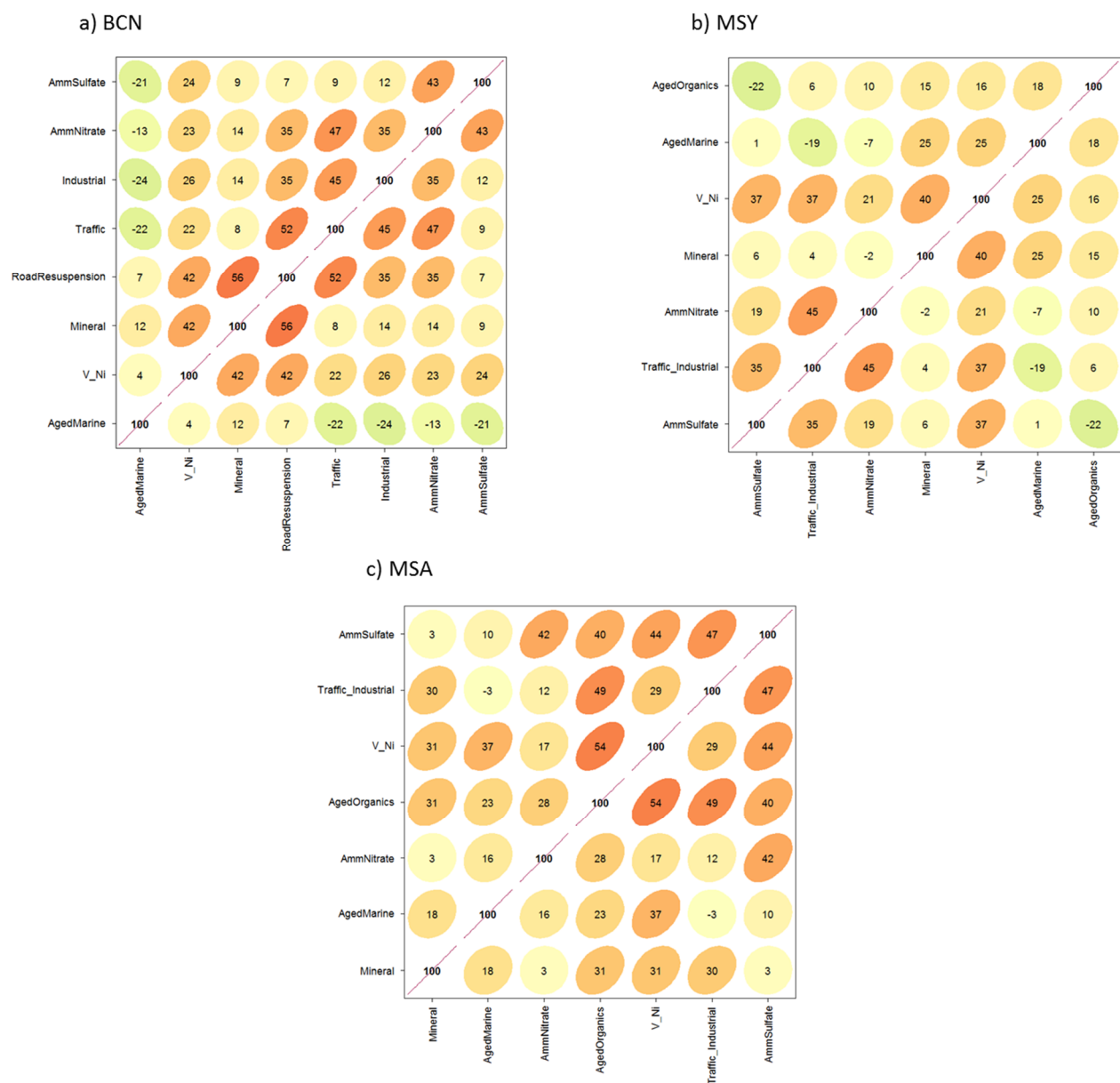


Figure 8

Supporting material



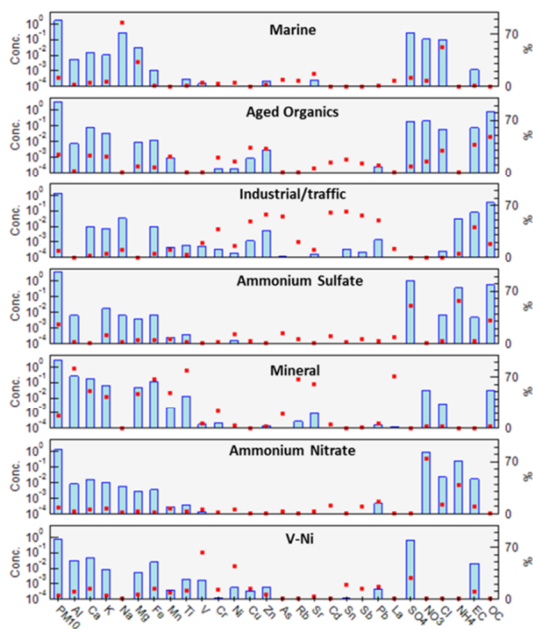


**Figure S1.** Correlation matrix between pairs of aerosol sources obtained by means of the PMF model at a) BCN, b) MSY and c) MSA. The correlation is coded by shape and colour for better visualization, lower correlations are represented by circles and lighter colours whereas higher correlations are represented by ellipses and darker colours.

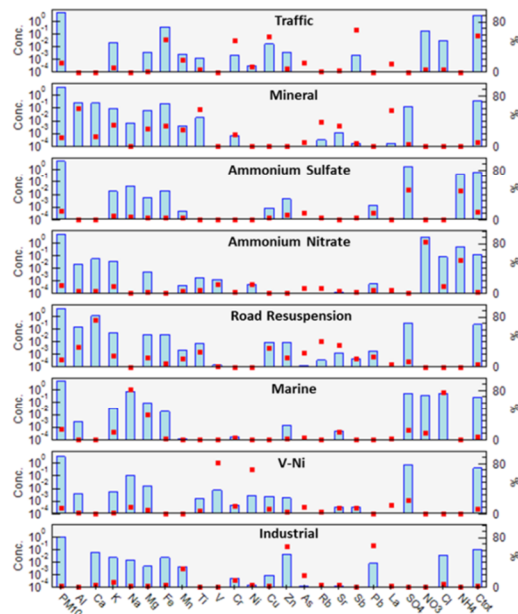


Legend: ■ % of Species  
■ Conc. of Species

## MSY



## BCN



**Figure S2.** Source chemical profiles obtained by means of the PMF model at MSY and BCN for the period 2004-2014 (Pandolfi et al., 2016).