

***Interactive comment on* “From air quality to climate: Impact of aerosol sources on optical properties at urban, regional and continental levels in the north-western Mediterranean” by Marina Ealo et al.**

Anonymous Referee #1

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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 (σ_{sp} and σ_{ap}). The

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aerosol source mass concentrations served as dependent variables and the σ_{sp} and σ_{ap} served as independent variables. Note that I am using the common symbols σ_{sp} and σ_{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 σ_{sp} and σ_{ap} contributions for each source type and summed the contributions to yield total calculated σ_{sp} and σ_{ap} . They then compared these calculated coefficients with measured σ_{sp} and σ_{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 σ_{sp} and σ_{ap} for pre-2010, when there were only mass concentration measurements (i.e. no σ_{sp} and σ_{ap} measurements). The reconstructed from σ_{sp} and σ_{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 specified 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 σ_{sp} and σ_{ap} ,

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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.

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 σ_{sp} , σ_{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 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. 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.

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'

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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'.

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.

- The abstract is too long and should be shortened.
- 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

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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.

- 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

- 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.

- P.6 Lines 19-24: "The three sites are involved in the Catalonian 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 Catalonian 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.

- 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's usage of past tense to describe the current study. I recommend consistent usage of present tense for this throughout the manuscript.

- P.7 Line 7: Include a reference for the protocol. There are MANY other instances in

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the paper where the authors make mention of protocols without providing references.

- 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; ...).

- P.10 Line 7: Change 'PM10 levels' to "PM10 mass concentrations".

- P.10 Line 10: Change "PM10 load." To "PM10 mass concentrations". Please do this for all instances in the manuscript.

- 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.

- 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.

- 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

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reword this assertion to better reflect the data in Fig.3.

- P.12 Lines 14-16. This has already been mentioned more than once so the sentence should be deleted.
- 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.
- P.12 Lines 17-24. This passage has already been discussed in previous sections and is not a result. Therefore, it should be deleted.
- P.13 Line 2: Change the word 'coefficient' to 'MSE'.
- 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.
- P.14 Line 19: Please clarify what you mean by "European scenarios".
- 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

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light scattering attributed to ammonium sulfate is highest in Aug-Sept and lowest in Nov-Dec.

- 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.
- 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.
- 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.
- P.15 Lines 26-27: "As a summary, we have shown that the main target pollutant

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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.

- P.16 Line 1: Please remove the phrase “As a novelty;”.
- P.16 Line 19: What ‘published results’? Please cite reference(s) to support this.
- 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.
- P.17 Line 5: The slope of modeled versus measured SSA is 0.80, which is not close to 1. Please reword this.
- 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”.
- 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.
- 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 5 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.

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- 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.
- 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.
- 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.
- 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.
- 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.

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- 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.

- 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.

- 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.

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Interactive comment on Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-217, 2017.

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