

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

General comments:

1. Organization

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

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

Figure S1: geography/topography of the two sites

Figure S4: relative concentrations

Figure S5: air mass origins and their seasonality

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

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

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

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

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

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

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

2. Methodology:

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

Another issue is the fact that averages are compared, but much of the discussion is rather qualitative (“lower” and “higher” concentrations). Standard deviations are rarely given or

commented on; the statistical significance of the many differences between averages (even when one average is only “slightly higher” than another) is not stated.

3. Geographic terminology

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

4. PM10 vs. PM1

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

5. Language

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

Examples:

Abstract line 6: “Differences on”,

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

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

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

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

p. 16020 line 1: “opposite to”

Specific comments:

Section 1:

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

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

Line 27: sufficient for what?

p. 16004 line 15: Please provide a reference.

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

Section 2.2:

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

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

Section 3.1:

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

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

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

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

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

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

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

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

p. 16010, Line 7: “However,,: This qualifier is not needed, as no one would expect PM1 to be driven by the dust suspension discussed in the previous sentence.

Line 22: “Saharan dust particles” are cited as a reason for “higher PM” concentrations at MSC compared to Puy de Dome and Jungfraujoch: Please specify: PM1 or PM10? In the long-term average, or episodically? It would be surprising if dust particles are the reason for higher PM1 concentrations. Geographical differences could be responsible, too, at the very least for the comparison with Jungfraujoch, which likely spends more time in the free troposphere than MSC, due to its much higher altitude.

Section 3.2:

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

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

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

Section 3.2.1:

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

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

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

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

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

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

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

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

Section 3.2.2:

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

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

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

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

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

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

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

Line 10: It is not clear how an impact of shipping emissions is visible in Figure 3, or which air mass is even talked about. MED? Again, the discussion of absolute concentrations is problematic here: Can the advection of shipping emissions in presumably otherwise relatively clean marine air really lead to an increase of absolute SO₄ concentrations on land? If so, can you provide a reference? The statement is at odds with a statement in the same section (previous page, line 25) stating that the sea breeze has a “clean-up” effect.

Section 3.2.3:

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

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

Line 14: Shouldn't this show in a similar seasonal cycle of NH₄ and SO₄ at MSY? This does not seem to be the case (Figure 2).

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

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

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

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

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

Line 10: see my comment on shipping emissions above.

Section 3.2.6:

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

Section 3.2.8:

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

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

Section 4.

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

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

Line 8: relatively high compared to what?

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

Figures:

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

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

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

Figure S3: How representative are these model calculations for the actual local BL development at the stations? BL development, particularly in mountainous regions and with respect to aerosol transport, is a local process, governed by the local topography at a scale below the resolution of many models. What grid resolution was the HYSPLIT model run on? Has the BL development at MSC and MSY been studied in terms of local measurements (local meteorological parameters, soundings, tracers, etc.)?

Technical corrections:

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

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

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

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

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

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

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

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

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