

# Interactive comment on “Vertical and horizontal variability of PM<sub>10</sub> source contributions in Barcelona during SAPUSS” by M. Brines et al.

## Anonymous Referee #1

### General comments

The manuscript presents interesting results on the spatial distribution of PM<sub>10</sub> chemical species and sources in Barcelona. Although many studies have been carried out in this area, these data are useful for improving the understanding on PM vertical and horizontal variability. In general, the work has been carried out correctly and well presented, results are sound and data interpretation is reasonable. Some criticisms may be however identified, as described in the following.

Response: We acknowledge the reviewer's positive general opinion of the paper and the criticisms have been addressed accordingly as shown below.

### Specific comments

In the calculation of the mineral matter mass (pag. 33339) Si and Al contributions are included using their main oxide form (Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>) and Ca as Ca carbonate: why the contribution of the other crustal elements (Na, Mg, K and Fe) is calculated just summing up their concentrations, without any correction for uncounted Oxygen or carbonate mass?

R: This is due to Si and Al being found mainly in the form of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>. The calculation of Al<sub>2</sub>O<sub>3</sub> from Al is made taking into account the molecular weight. Owing to sampling in quartz fibre filters, the SiO<sub>2</sub> concentration is calculated as 3·Al<sub>2</sub>O<sub>3</sub>. Mineral matter is now calculated as the sum of SiO<sub>2</sub>, CO<sub>3</sub><sup>2-</sup>, Al<sub>2</sub>O<sub>3</sub>, nss Ca, Fe<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>O, and the oxides of nss Mg and nss Na. The manuscript and figures have been corrected accordingly.

Some more information on the robustness of PMF results should be provided: in source profiles, is the sum of the contributions of the chemical species (sum of fjk) minor of 1, and also close to 1 (as most of the aerosol species have been measured)? Is the PM<sub>10</sub> mass well reconstructed by the model?

R: The sum of the contributions of the chemical species for each source is shown in the following table, being most of them close to 1. The value for road dust (>1) might be due to an overestimation of SiO<sub>2</sub> and CO<sub>3</sub><sup>-</sup> from Al and Ca. In fact SiO<sub>2</sub> and CO<sub>3</sub><sup>-</sup> sums up 65% of the road dust profile.

Table S2: Sum of the chemical species contributions to each PMF factor.

Exhaust & wear	Road dust	Mineral	Aged marine	Heavy oil	Industrial	Sulphate	Nitrate
0.83	1.17	0.76	0.89	1.00	0.59	0.79	0.89

The PM<sub>10</sub> mass is well reconstructed, as the residuals represent only 8% of the PM<sub>10</sub> mass (see Table S3). In addition the plot of the modelled versus the observed PM<sub>10</sub> concentrations has resulted in a R<sup>2</sup>= 0.93 and a slope of y=1.03x-0.80, confirming the good agreement between the PMF results and the observed concentrations.

Table S2 and Figure S1 have been included in the supplementary information and the following text has been added to the manuscript:

“The PMF result has proven to be very robust (the sum of the contributions of the chemical species for each source are close to one, see Table S2) and the PM<sub>10</sub> mass has been well reconstructed by the PMF model (see Figure S1).”

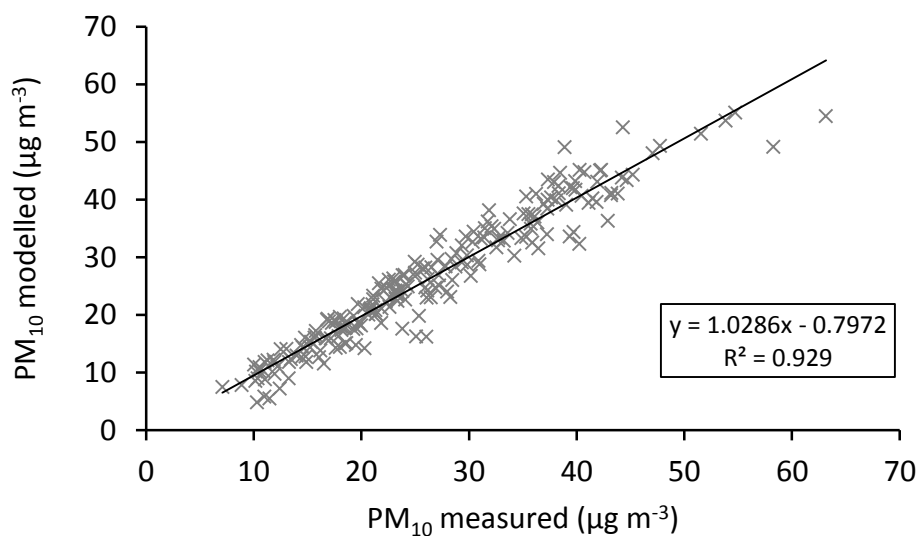


Figure S1: Modelled (by means of PMF) versus measured PM<sub>10</sub> concentrations.

Which are the chemical species included in the PMF? I imagine they are those reported in Figure 4, but I do not understand “SiO<sub>2</sub>CO<sub>3</sub>”.

R: The chemical species included in the PMF are those reported in Figure 4 and Table S3. SiO<sub>2</sub>CO<sub>3</sub> refers to the sum of SiO<sub>2</sub> and CO<sub>3</sub><sup>2-</sup> compounds. To avoid any confusion it has been modified in the above mentioned Figure and Table to “SiO<sub>2</sub>+CO<sub>3</sub>”.

The discussion on the spatial distribution of the mineral component is a bit confusing: at the beginning it is shown that calculated mineral matter and crustal tracers (Ti, Rb, Li, which also characterize the mineral PMF factor) are higher in the RS and UB sites with respect to the tower sites, then a very homogenous contribution of the mineral factor is found. I understand that the calculated mineral matter also includes contributions of road dust, but I think this point needs some more explanations especially for what concerns the specific mineral tracers. May the contributions of SO<sub>4</sub>, OC and EC in the profile of the mineral factor have been overestimated by PMF (thus overestimating also the homogeneity of the spatial distribution)?

R: Indeed, we attribute the different spatial distribution of the calculated mineral matter and the mineral factor to the contribution of the road dust to

the first one, causing an increase in concentrations at the RS and UB. Still the PMF mineral factor shows an important enrichment in S and C with respect to the average crust composition (Taylor, 1964 and Mason, 1966) indicating the mixing of mineral dust with regional/local plumes and the neutralization of sulphuric acid by mineral cations through heterogeneous reactions. We have highlighted this in the text.

As the sampling at the ground level are not in the same place of those on the towers, some caution should be played in the attribution of observed effects to the altitude, as they could be simply due to the different (horizontal) location. For example, it is commented that the impact of the industrial factor is higher at the ground level: is not the position of the UB (closer to the industrial area) more relevant than the altitude? Moreover, the distribution of nitrates is in my opinion more correctly described when discussing the concentrations in the 4 sites (pag. 33348, lines 7-10), highlighting that nitrate decrease with the distance to traffic sources, than when summarizing that their contribution is slightly higher at the ground (pag. 33348, lines 27-29).

R: The referee is correct when we compare UB site with TM, but our conclusion is still valid if we compare UB with TC, which is the closest site to the metallurgy cluster (12.1 km).

The sentence in lines 27-29 of page 33348, has been deleted.

The sentence “this statistical tool is usually unable to differentiate between natural and anthropogenic sources contributing to the same factor” seems a bit tautological (if they are within the same factor they are not separated by definition). It would be better to say that PMF may not be able to separate similar sources and, due to chemical reactions, apparently “natural” PMF factors like mineral and sea salt may also include anthropogenic contributions.

R: We agree with the referee, and re-phrased the sentence:

“However, PMF may not be able to separate similar sources and, due to chemical reactions, apparently “natural” PMF factors like mineral and sea salt may also include anthropogenic contributions.”

To this regard, did the authors try to increase the number of factors? What happens with 9 factors?

R: The PMF solutions with nine factors showed the same factors shown with the eight solution, with an additional nine one called "Se-SUL", composed mainly of Selenium and Sulphate (see Figure S5) and lacking of any clear temporal trends.

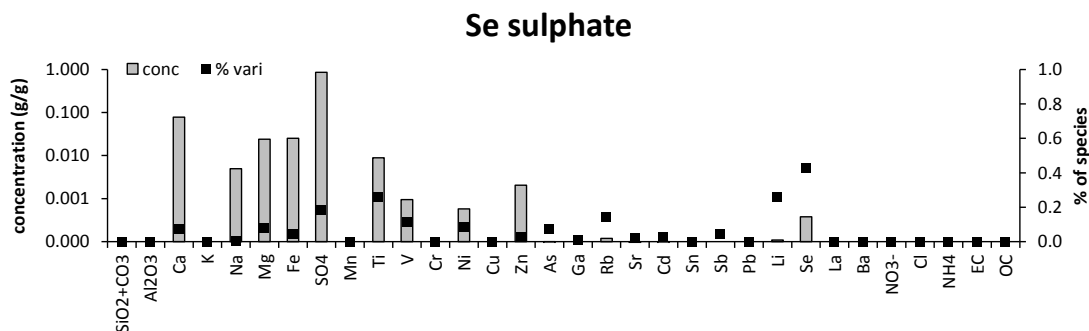


Figure S5: PMF profile of the Se sulphate factor.

Table S4 shows that most of the factors were broadly conservative. In some stations (TM, TC) the road traffic, mineral and vehicle exhaust and wear are mixed up. The eight factor solution was found more appropriate.

This analysis has been incorporated to the supplementary information and also to the manuscript:

“A nine factor solution was attempted and showed the same factors shown with the eight solution, with an additional nine one called "Se-SUL", composed mainly of Selenium and Sulphate and lacking of any clear temporal trends. (see supporting information).”

Table S4: Temporal correlation coefficients for the factors found in the 8 and 9 factor solution.

8 factor PMF solution	RS	UB	TM	TC
	Correlation with same factor found in the 9 factor solution			
1 Vehicle exhaust and wear	0.9	0.6	0.6	0.4
2 Road dust	0.9	0.5	0.5	0.4
3 Mineral	0.7	0.8	0.6	0.6
4 Aged marine	0.9	0.8	0.9	0.7
5 Heavy Oil	0.9	0.8	0.6	0.7
6 Industrial	0.9	0.6	0.7	0.7
7 Sulphate	0.9	0.8	0.8	0.9
8 Nitrate	0.9	0.8	0.8	0.7

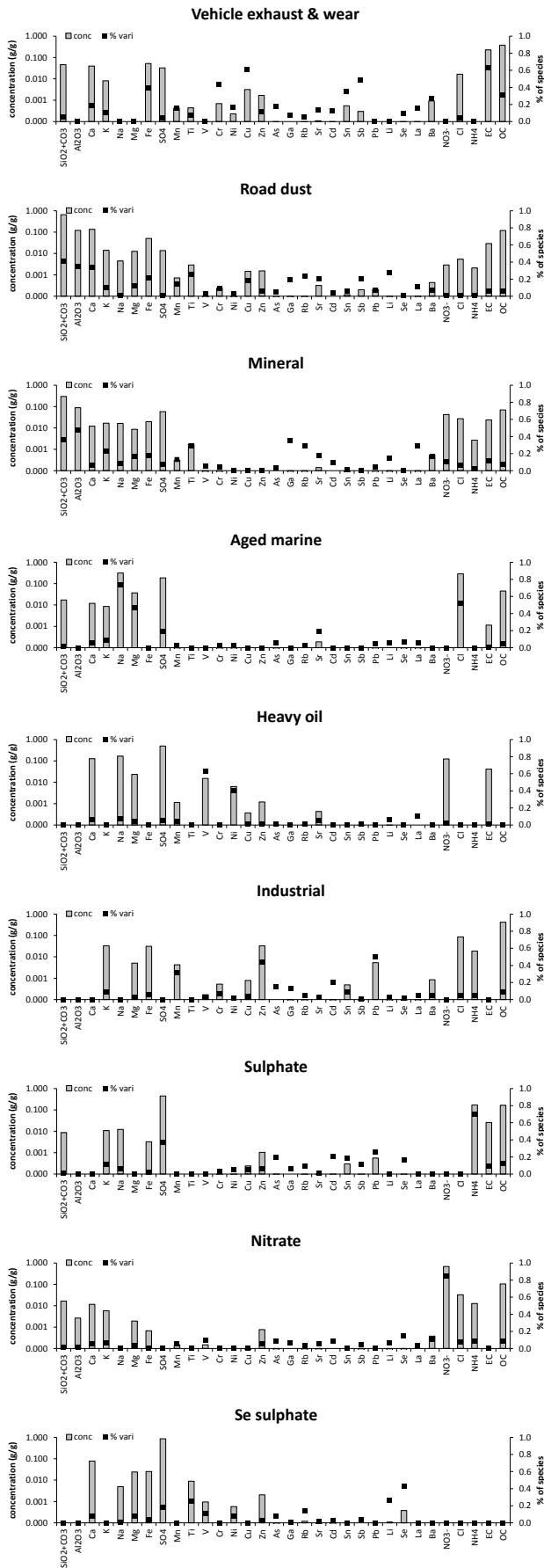


Figure S6: Profiles of the each PMF 9 factors solution.

Also, how robust is the presence of sulfate in the mineral and sea factors? Did the authors try to pull down this contribution? To evaluate the aging of the sea salt source it would be important to say which is the Na/Cl ratio in the profile of this source.

R: The interquartile range of sulphate concentrations in bootstrap runs is 12.9-14.4% in the sea salt factor 8.9-10.9% in the mineral factor, containing in both cases the concentration of our final solution. Therefore we believed that the solution was quite robust and did not try the pulling down

The Cl/Na ratio in the sea salt factor was 0.91, significantly lower than the value of 1.80 reported for sea water by Henderson and Henderson (2009), indicating atmospheric aging of sea salt particles, with formation of sodium sulfate and depletion of chloride.

We have included both statements in the text.

The description of the method used to calculate the fresh marine and the anthropogenic marine sulfate contribution (pag. 33354, lines 19-22) is not very clear.

R: The fresh sea salt is calculated as the sum of  $ssNa + Cl^- + ssMg + ssCa + ssSulphate$ .  $ssNa$  is calculated as the measured  $Na - nssNa - Na$  from  $Na_2SO_4$  in the PMF aged marine factor.

The anthropogenic marine sulphate is calculated as the difference between the PMF aged marine and the fresh sea salt.

We have clarified this in the text.

Technical corrections

- Although reported in other SAPUSS papers, a map of sampling sites would be useful

R: Given that this paper is part of a Special Issue it was decided to include a map with the locations of the sampling sites in the introduction paper by Dall'Osto et al. (2013) in order to avoid repetition in every resulting paper. In Figure S3, the polar plots are shown on a map for each PMF factor at each site, which indicates the location of each site in the urban agglomerate.

- Graphs in Figures 3 and 4 are too small.

R: We will make sure these Figures are legible in the final manuscript.

- pag 33343 line 22: check parenthesis position.

R: It has been checked and corrected.

- pag 33344 last two lines: the verb is missing, and it is not clear to which profile this constrain was applied (mineral?)

R: The ratio was applied to the mineral factor. We have revised the sentence.

- pag 33348, line 4: “evidencing that THESE sources” instead of “ITS sources”

R: Is has been corrected.

## **Anonymous Referee #2**

Objective: The objective of this work was to assess the vertical and horizontal variability of aerosol levels and composition, sources contribution and physico-chemical transformations in Barcelona.

Structure: The paper is clear and well structured. It has a correct English.

R: We thank the referee for believing that the paper is clearly organised.

Innovation: Neither the analytical techniques and models used in the paper are innovative, nor their application to the city of Barcelona, which is one of the most studied cities in Europe in this field of science. However, I agree that there are very few studies conducted in European urban vertical columns specifically looking at chemically resolved aerosol sources.

R: As the referee mentions, many studies have been carried out in Barcelona and the Western Mediterranean Basin, but few of them have focused on the vertical variability of aerosol concentrations and their chemical speciation. Our paper aims at addressing this specific gap of knowledge.

Introduction: The introduction gives a good state of the art concerning the developed work and clearly presents the objectives of the study.

R: We thank the reviewer for his positive comments.

Methodological approach: From my point of view the major constraint of this work is the sampling design to test the hypotheses which are subjacent to this work. Authors aimed to study the vertical profile of the aerosols composition and sources, however sampling points varied not only in altitude but also horizontally. Consequently, the differences between factor contributions to PM10 in ground and tower levels can be due to the sources affecting each one of the coordinates and not to vertical issues. To properly achieve the proposed objectives, authors should have sampled in parallel at different heights for the same coordinate.

R: The reviewer is correct stating that the simultaneous sampling at ground levels of the tower sites (especially TM) would have resulted in a more complete study of the vertical variability at these locations, but due to logistic reasons this was not possible.

At the same time authors stated that a decreasing trend from the site closest to traffic sources to the one located in the suburban background was observed. In this case authors refer to a horizontal profile and therefore they

should have kept the altitude constant. Authors should comment this constraint.

R: The reviewer is right that stating that there is a decreasing trend from sites closest to traffic to the more distant ones is not accurate, as two of the sites are located on ground levels while the other 2 are located at a certain height. Therefore a clear distinction has been made through the manuscript separating the sites at the same level (ground sites RS and UB and tower sites TM and TC).

Results: -A map with the location of the sampling points, wind rose and trajectories representing each trajectory cluster should be added to support the interpretation of the results.

R: Given that this paper is part of a Special Issue it was decided to include a map with the locations of the sampling sites in the introduction paper by Dall'Osto et al. (2013) in order to avoid repetition in every resulting paper. Nonetheless in the supporting information in Figure S3 the different PMF factors Polar plots are presented in a map for each site, which indicate the dominant wind direction when the highest concentrations of each factor at each site are recorded. This figure is used in the results and discussion sections to support the interpretation of the results.

-Figure 2 doesn't add new information to Table 1.

R: We have removed Table 1.

-The authors should give more information about the constraints used for the source apportionment PMF to quantify the road dust fraction of the mineral dust.

R: The road dust emission profile was introduced by means of auxiliary equation (pulling equations, Paatero and Hopke, 2008), consisting in pulling a  $f_{jk}$  toward the specific target value  $a$ :

$$Q_{aux} = \frac{(f_{jk} - a)^2}{\sigma_{aux}^2}$$

where  $\sigma_{aux}$  is the uncertainty connected to the pulling equation, which expresses the confidence of the user on this equation. In the present study, a pulling equation was used for each specie in order to pull concentrations of a factor toward the target concentration in the road dust emission profile as obtained by Amato et al, (2009). An average profile of 4 road dust samples collected at 4 different points of the Diagonal Avenue was selected as a representative emission profile.

This text has been included in the manuscript.



Conclusion: The conclusion reflects the main outputs obtained in the developed work.

R: We thank the reviewer for his comments and suggestions, which have been implemented to the best of our abilities and have improved the quality of the manuscript.

#### References:

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