Oxidative potential apportionment of atmospheric PM$_1$: A new approach combining high sensitive online analysers for chemical composition and offline OP measurement technique

Response to the reviewer #2:

We thank the reviewer for the additional feedback. See bellow our responses to the comments (in blue).

The authors replied pertinently to the first critical point arisen during the first revision step regarding the OP results interpretation and representativeness. A deeper discussion of the results and limits of this approach has been included in the revised manuscript version. From this point of view the new version of the manuscript addresses the concerns emerged in the first revision step. The second critical point I rose concerned the justification of the adoption of PMF 2 as source apportionment strategy rather than merging all the raw data into a unique input dataset for the source apportionment. The consideration of the first reviewer who suggests for the metals source apportionment that the prior grouping of the variables into 5 factors decreases the information for the PMF-PM1 and makes interpretation more difficult applies also for the OA source apportionment. Since no previous publications compared the two approaches, we don't have a feeling on whether the two methodologies provide comparable results or not. No standard approach has ever been fully defined to treat multiple datasets for a comprehensive PM1 source apportionment, although many studies merge ab initio the raw data from different instruments to form a unique input dataset for source apportionment. For this reason the adoption of a PMF 2 approach is a relatively new approach and its adoption has to be well justified. The authors mentioned that a comparison between the two methodologies goes beyond the scope of the paper, on the other hand the multilinear regression of OP is based on PMF results, therefore the choice of the source apportionment strategy is critical for the purpose of this paper. For this reason I would recommend a comparison of the two approaches to be reported at least in the supplementary information, as already done by running a PMF on OA factors and metals. As mentioned by the authors, there can be several ways of combining datasets to perform a PM1 source apportionment, however they could be bracketed by two extreme approaches:
- The first approach is PMF2, where source apportionments are performed on the individual datasets and the obtained factor time series are utilized as inputs for a comprehensive PM1 source apportionment.
- The second approach is to merge all datasets before the source apportionment and perform a unique PMF.
The authors mentioned that the PMF 2 approach enables a more accurate identification of secondary aerosol sources which, from previous publications, are considered relevant contributors of OP, nonetheless the secondary factors resolved are identified as AS-rich and ON-rich, which are similar to the typical factors identified from ACSM OA datasets: usually MOOA (or LVOOA) correlates with SO42- and LOOA (or SVOOA) correlates with NO3-, therefore the resolution of similar SOA factors can be achieved without necessarily adopting a PMF 2 approach. The authors also mentioned that SOA factors resolved by ACSM data are usually reported as either a single factor or two factors separated by their degree of oxygenation (LOOA/MOOA) rather than in terms of sources, nonetheless also the sources of the resolved AS-rich factor and ON-rich factor are not clear: the two factors are characterized by high contributions of SO42- and NO3- respectively, therefore also the ON-rich and AS-rich factor are resolved by the chemical-physical processes involved in the SOA formation/aging rather than by their origin.

Response: We understand the reviewer's concern about the PMF methodology. In response, we performed the suggested PMF by combining all datasets prior to analysis, including the organic fragments (from m/z 12 to 100), metals, BC fractions, NO3, SO4, NH4 and Chl. The data inputs were previously averaged on a similar 1h-time step. The resulting factors profiles are presented in Figure

A1. This approach could retrieve only 7 sources, and increasing the number of factors did not lead to physically reasonable solutions.

We successfully identified similar factors than previous methods, with consistent R^2 correlations: shipping (0.77), dust resuspension (0.99), industrial (0.80) and AS-rich (0.97). However, the identification of the 3 other factors remains challenging. The 5th factor was characterized by an organic m/z spectra showing a high affinity with the MOOA profile (Figure A2) and some elements which were present in the regional background profile from the PMF_{metals} (Br, Sn, K). The 6th factor presented a moderate correlation with the ON-rich factor from PMF^2 approach ($R^2= 0.67$) but unexpectedly featured a high contribution of BC_{FF} which might be due to some mixing of this factor to traffic.

The last factor is interpreted as a result of the mixing of traffic and cooking sources. This lack of clear separation is attributed to the very similar mass spectra profiles of HOA and COA for the organic fraction (Figure A2), which are difficult to deconvolve without applying specific constraints (Chazeau et al., 2022; Chen et al., 2022). The mixing is also visible in the factor's diurnal evolution with unseparated morning and mid-day peaks (Figure A3). Note that the biomass burning source was not resolved in this solution.

The description of this PMF approach is now reported in the supplement (in "PMF_{PM1} with organic m/z fragments + metals + ions + BC dataset" section), with Figure A1 presented as Figure S19. Additionally, the following sentence has been added to the main text (line 536): "A PMF analysis was also conducted on all instruments datasets (i.e. organic fragments from m/z 12 to 100, ACSM inorganic species, BC fractions and metals) merged into a unique input matrix and didn't result in a satisfactory solution (see the supplement section and Figure S19)."

We agree with the reviewer that the resolved AS-rich and ON-rich factors from the PMF^2 approach are resolved based on chemical-physical processes rather than specific origins. However, as stated in our previous response, MOOA and LOOA are not exclusively correlated to sulfate and nitrate, and therefore attributed to the AS-rich and ON-rich factor, respectively. The PMF^2 method enabled the attribution of non-negligible SOA fractions to cooking, traffic and biomass burning as well. Furthermore, it allowed a clear separation of traffic, cooking and biomass burning sources which was not achievable with the method merging all datasets before the analysis. However, this method warrants further development by including additional data (i.e. additional metals and time periods) and using appropriate constraints to enhanced the solution.
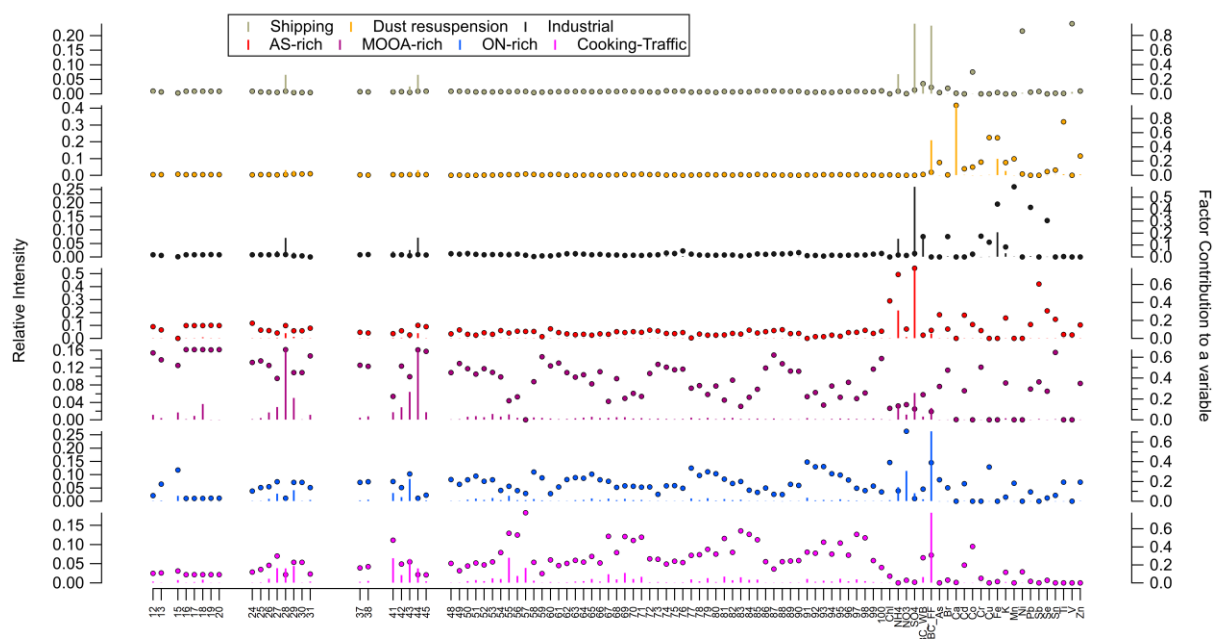
Figure A1- *Factor profiles from the PMF solution using organic m/z fragments, ACSM inorganic species, BC and metals as inputs. The sticks represent the normalized contribution of the variable to the factor (left axis) and markers show the normalized factor contribution to each variable (right axis).*
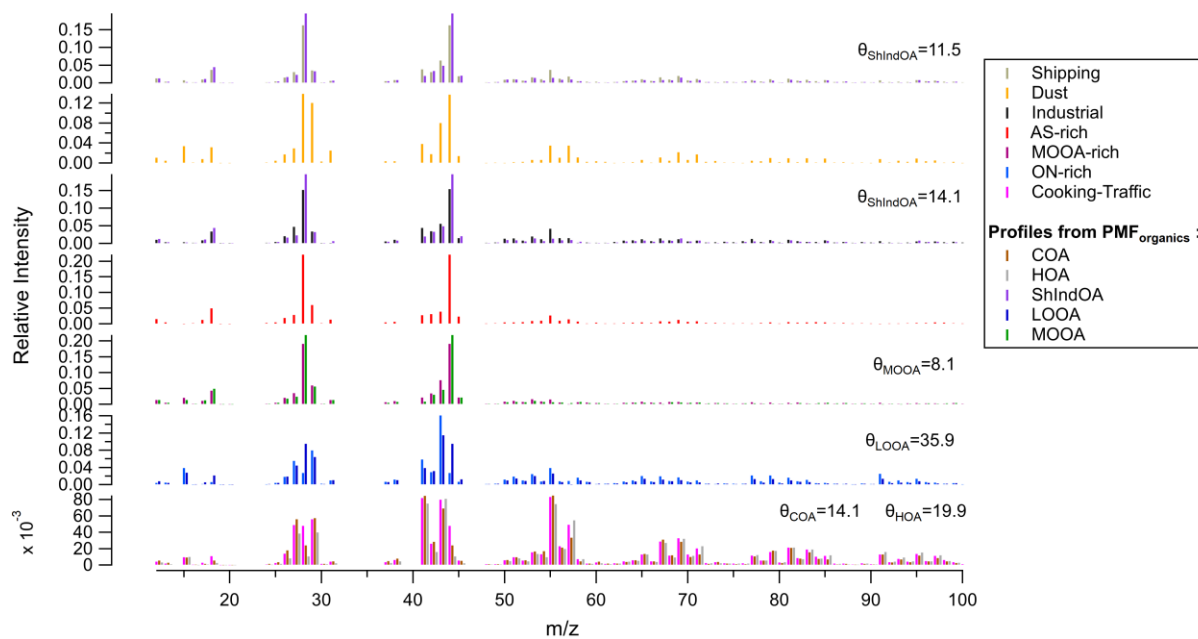

Figure A2 *– Organic fractions of the factor profiles from the PMF solution using organic m/z fragments, ACSM inorganic species, BC and metals as inputs. The profiles are normalized by the sum of organic m/z to compare with OA mass spectra from the PMF$_{organics}$ solution. The angles θ=arccos(R) (in degrees) are given to evaluate the similarity between mass spectra, with lower angles corresponding to higher similarities.*
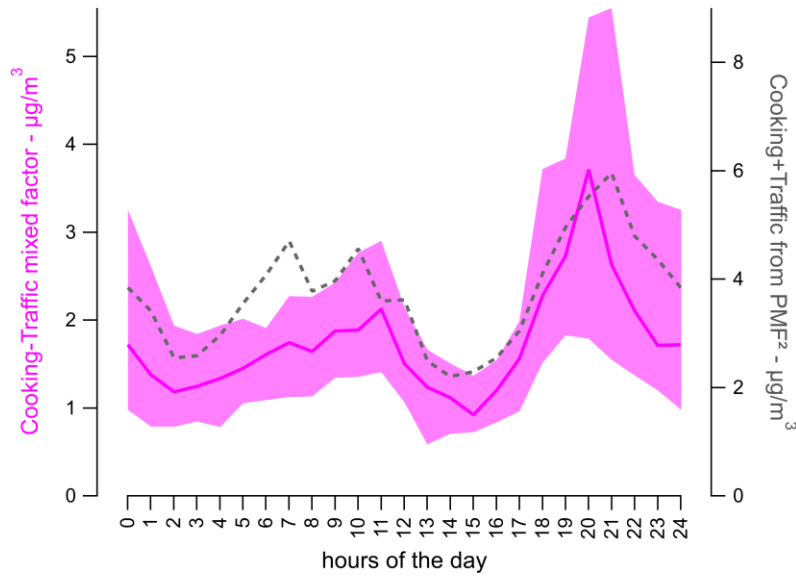
***Figure A3** – Average diurnal profiles for the mixed cooking-traffic factor and the sum of cooking and traffic factors from the PMF² solution.*

Minor comments:

I would remove the sentence at line 482 "Similar contributions were found in another Mediterranean coastal city, Barcelona (4%; Via et al., 2023), and in some French urban sites in the vicinity of an industrial area (Weber et al., 2019)." because it compares the contribution of industrial factors found in different cities, which can be related to different industrial processes and the similar low contributions found can be just casual.

Response: We deleted this sentence as suggested.

Sentence at line 368 "those found by in 't Veld et al., (2023) on PM1 all year long in": I think there's a typo "'t"

Response: This is actually the author's name: "Marten in 't Veld".

References

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