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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Source apportionment of highly time resolved trace elements during a firework episode from a rural freeway site in Switzerland" *by* Pragati Rai et al.

Anonymous Referee #3

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The paper "Source apportionment of highly time resolved trace elements during a firework episode from a rural freeway site in Switzerland" by Rai et al. deals with Positive Matrix Factorization analysis of a dataset of 1-h resolved trace elements. Despite the authors declare the existence of much more information on high time resolved scale (mass concentration by TEOM, equivalent black carbon by MAAP, ACSM data), they carried out the analysis on elements only. This limits strongly the information provided by the study (e.g. they can apportion only the mass related to elements, that they estimated to be about 20% of PM10 mass). Thus, the results cannot be representative of the total contribution of the sources to the measured PM. Furthermore, lots of constraints were implemented to reach the final solution. In some cases, both source

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Discussion paper

profiles and temporal trends were constrained. So many constraints to the model make questionable the validity of the results, also considering that these constraints are not adequately supported by a methodological description of the way they were obtained, as explained in more detail below. Whether the paper is well structured and well written in most parts (even if some obscure descriptions remain), the scientific aspect is not fully convincing.

Major concerns

Page 5, line 15: excluding mass data (mentioned at p.4 l.2) should be carefully discussed as it strongly reduces the interest of the results, preventing an absolute quantification of the factor contributions to the measured PM. Furthermore, maybe the authors decided to analyse separately ACSM data, but at least equivalent BC information could be of help in source resolution.

Page 6, lines 11-12. “The unconstrained PMF solutions yielded mixed factor solutions. Therefore, it was essential to constrain specific factor profiles and the time series in the PMF analysis to avoid mixing (see details in the Supplement, section S1, Fig. S1)”. This is the weakest aspect of all. The way in which the factor profiles/time series are constrained is the key point for all the rest of the analysis. Constraints determination strongly affects the final results (see described differences between the preliminary analysis and the constrained one) and merits detailed description and attention. Opposite, its description was moved to the Supplemental Material, and what is reported there is anot sufficient to determine the robustness of the approach. The following information should have been provided: 1) How many factors were present in the final analyses of the fireworks and non-fireworks periods? 2) Were the sources other than fireworks and sea-salt comparable between the datasets? (In terms of profile and tracer species?) 3) Were 2 firework-related factors identified in the analysis of the firework-days subset? 4) What about the residual of S in the unconstrained 9 factor solution? 5) The need to constrain both profile and temporal trend of the sulphate source is very suspicious (the whole “secondary sulfate” factor was constrained in the final

solution).

Pag 6, line 13: “obvious structure”: completely obscure what the authors mean.

Pag 6, line 28: “both the sea salt and secondary sulfate factor time series were also constrained with a-value 0.01”. Further constraint implemented. Please note that a small a-value was used. Is it consistent with uncertainty estimates for the non-firework sub-set and for the sulfate factor identified in the preliminary 9-factor solution? Please also note that the constraints come from two different analyses.

Page 7, line 19: obvious. It was checked in the preliminary analysis at 9-factors and then constrained both as far profile and temporal patterns are concerned in the final solution.

Page 8, “Fireworks” paragraph. Considering that the fireworks profile was constrained, it sounds very strange that two fireworks sources were identified in the final analysis. As previously required, the existence of two fireworks sources should be supported by their identification at least in the unconstrained analysis of the fireworks period. If not, the strength of the imposed constrain should be verified to get if it artificially generates the presence of two factors.

Page 9, lines 1-4 and Figure 4. Completely obscure. I interpret “normalized” as “divided by”, but in this case how can the negative values be justifiable? Furthermore, what is “composition”? Average contribution of the factor to each element?

Page 11, lines 22-23: “We established that data sets including extreme events such as fireworks can be apportioned by ME-2 without disturbing the model solutions”. Untrue. The imposed constraints completely modified the output of the unconstrained analysis.

Minor comments

Page 2, Line 12: A reference to: “Fe in brake lining can reach up to 60 % by weight” is needed

Page 2, line 27: add “among others” after “Wang et al., 2018”. Indeed, the list is far from being complete (see e.g.: Li et al. 2017 http://dx.doi.org/10.1016/j.jenvman.2017.02.059; Zhou et al., 2018 https://doi.org/10.5194/acp-18-2049-2018 among the most recent). If the authors intend providing a full list, a much more detailed research has to be done.

Page 3, lines 10-12. “The later, being essential in particular when separating extreme events such as fireworks which are most often excluded from the PMF input matrix (Ducret-Stich et al., 2013; Norris et al., 2014) to avoid distortion in the PMF solution due to unusually high emissions”. This sentence is questionable. As reported by Paatero et al., (doi:10.5194/amt-7-781-2014) wrong decision on the outlier status of data can introduce serious modelling errors. Please also note that opposite to what stated by the authors, examples in the literature tried to exploit fireworks tracers to quantify the source contribution, with different approaches (e.g. Scerri et al., 2018 https://doi.org/10.1016/j.chemosphere.2018.07.104, Ji et al., 2018 https://doi.org/10.1016/j.scitotenv.2018.01.304, Vecchi et al., 2008 http://dx.doi.org/10.1016/j.atmosenv.2007.10.047)

Page 7, line 28: “absolute mass”. It should be recalled that it refers only to the mass related to elements, as no PM mass was inserted in the analysis.

Page 9, line 25-26: “The two dust factors together explain 95 % of Ca, with no other factor explaining more than 93 %”. Obscure. If already explained at 95%, how can other factors explain Ca for more than 93%?

Page 9, lines 29-30: “In general, Ca is commonly associated with 30 mineral dust, construction activities, vehicular emissions and iron/steel plants”. References are needed.

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