

Interactive comment on “Submicron aerosol source apportionment of wintertime pollution in Paris, France by Double Positive Matrix Factorization (PMF²) using Aerosol Chemical Speciation Monitor (ACSM) and multi-wavelength Aethalometer” by J.-E. Petit et al.

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The authors are grateful to Referee#1 for all comments and suggestions.

We fully agree with Referee#1 that a single PMF analysis including organic m/z fragments, inorganic ions and BC fractions should theoretically “better serve science”, as the very large diversity of organic fragments is expected to provide much more informa-

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tion compared to the use of only few OA factors. Such an approach has been previously considered in our work, but did not provide satisfactory results. Indeed, from Q/Q_{exp} and bootstrap calculations, this single PMF analysis only led to a 3-factor solution, with ammonium nitrate-rich and traffic aerosols gathered in one factor (as shown in Fig. AC1 and AC2) while results obtained for a higher number of factors did not allow for the determination of a stable solution (Fig. AC3). Residuals from this single PMF analysis were also examined in terms of contribution of variables to the Q/Q_{exp} ratio. Each variable displayed equivalent contribution (i.e. same order of magnitude), but due to the greater number of variables referring to each OA fragment, the latter contribute up to 95% of the total Q/Q_{exp} (Fig. AC4), indicating that this PMF analysis is mainly driven by OA fragments, regardless of the other variables (inorganic ions and BC fractions) that are very strong contributors to PM1. This is probably linked to a needed optimization of the error matrix, but this would also require assumptions. Indeed, one drawback of this single PMF approach is that the overall uncertainty matrix is not homogeneously constructed: the organic m/z error matrix (obtained from ACSM data processing Igor toolkit) was horizontally stacked with uncertainties from the Polissar approach for ions and BC fractions. This “weighing” issue has already been reported by Crippa et al. (2013), where AMS and PTR-MS datasets were combined for a single PMF analysis. It has been overcome by using a scaling value (c) in order to down-weight some variables. Although the used assumptions have been carefully framed, it still needs initial “guess-work”. The same occurred in our study. Each assumption (from the a-values used in the first PMF analysis, the number of organic factors, to the relative uncertainty of organic factors, inorganics and BC fractions) has been thoroughly tested, as described in the Supplementary Material. Results of these tests reinforce the fact that our PMF2 approach, as discussed in the manuscript, has been carried out using adequate parameters. However, as we proposed after Referee#2’s comments, we will add a “highlight” of the results of these tests in the revised manuscript.

Answers to specific comments:

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1) This is not real-time characterization of PM sources. Highly-time resolved? Possibly. But not real-time!

A: “Real-time” will be replaced by “highly time-resolved” in the revised manuscript.

2) Is $m/z=60$ indicative of wood-burning emissions? Please specify.

A : m/z 60 is commonly used as a biomass burning tracer (Aiken et al., 2009). The link of $m/z60$ with wood burning PM is highlighted here by a stronger correlation coefficient between $m/z60$ and BC_{wb} (0.73), compared to $m/z60$ and BC ($r^2=0.23$). This information will be added in the revised manuscript.

3) Is the assumption that only wood-burning contributes to BrC?

A : The Aethalometer model (Sandradewi et al., 2008) assumes that the enhanced absorption at near UV wavelengths is due to absorbing organic molecules (BrC) linked to wood-burning emissions (notably PAH and HULIS). To the best of our knowledge, there is no study in ambient conditions showing at near-UV wavelengths used by the Aethalometer significant absorption from BrC related to other sources than wood-burning.

4) While a slope of 0.99 is good, the somewhat lower correlation coefficient of 0.65 for ACSM+BC_{aeth} (I assume that is what is used for mass closure) against the TEOM even after averaging at 3-h resolution does not lend itself to the strong characterization implied by “validating”. Softer language should be used – perhaps couching the comparison in the language of instrument uncertainties (which have not been specified in the measurement section!)

A: “validating” will be replaced by “cross-checking”. It should be noted here that similar mass closure exercises have been carried out in different studies using ACSM and TEOM, which have shown results similar to ours (e.g. r^2 of 0.77, 0.68 and 0.71 in Carbone et al. (2013), Sun et al. (2012) and Budisulistiorini et al. (2013)). Uncertainties for TEOM range between 15 and 20% at 50 $\mu\text{g}/\text{m}^3$ (Le Bihan et al., 2005 and 2006).

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This point will be added in the manuscript.

5) Uncertainties seem large, but not clear what was the justification. For example, how was the 40% uncertainty for the two BC fractions derived – a propagation (e.g. “sum of squares”?) of uncertainties from the two papers mentioned? Why pick 50% for Potassium – how big are the measurement artefacts? Empirically-determining uncertainties for the ACSM data to ensure appropriate weighting for the organic fractions in later PMF analysis seems dubious. Were they set too low compared to the actual values, so as to get “good” PMF results?

A: The BC uncertainty is defined as the extended uncertainty according to Favez et al. (2009) and Sciare et al. (2011). A 20% uncertainty was assumed in this study, accounting for the Weingartner correction (Weingartner et al., 2003). In order to account for the uncertainty related to the Aethalometer model assumptions, this value has been multiplied by a factor of 2. The impact of the choice of relative uncertainty for each BC fractions (BC_{ff} and BC_{wb}) is described in Appendix E. Notably, Table E.1. shows that PMF₂ results using 20% or 40% rel. unc. for BC fractions are very similar. Note also that the OA rel. unc. was set from the same reasoning : a factor of 2 was applied to the rel. unc. of OA factors from a 15% uncertainty for OM (for instance, error at $m/z44$ represents 12% in average), since PMF outputs are expected to exhibit a higher uncertainty. Furthermore, a recent intercomparison involving 13 ACSMs was carried out in Paris (November-December 2013). The assumptions used here for the relative uncertainty of (in)organic species and OA factor concentrations are in good agreement with results obtained from this intercomparison (Crenn et al. and Fröhlich et al., to be published). For potassium, we agree that major artefacts may occur at $m/z39$, as organic species may contribute to this fragment (e.g. Ji et al., 2009), but are hardly quantifiable using unit-mass resolution ACSM data. For these reasons, we have used a rather high relative uncertainty (50%) for this compound. Finally, bootstrap analysis is indeed available in EPA PMF v3, but not within SoFi toolkit. Bootstrap creates a distribution in factor profiles that can be associated with model output uncertainty. Although

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being available for profiles, these results are not accessible for factor timeseries.

6) "OOA is found to significantly contribute to the traffic organic mass although its exact contribution cannot be determined without the much-needed thorough determination of uncertainties." – This undercuts the novelty of this PMF2 approach, and discounts the next statement that this PMF2 methodology is "especially efficient" in linking OA factors and pollution sources.

A : We agree that the take-home message of this sentence is too strong compared to the benefit of the PM2 methodology. The contribution of OOA to traffic organic mass is somewhat linked to the relative uncertainty of OA factors used in the second PMF analysis. As described in Appendix E, the 30-40% range gave most satisfactorily and similar results. Discussion will be changed in the revised manuscript.

7) The EPA's PMF model allows boot-strapping techniques. Yet, authors finish by saying the results need to be refined using boot-strapping of OA factors. There is not a significant discussion of the effects of boot-strapping in the main text, if that was indeed utilized to obtain the results in this manuscript.

A: Bootstrapping can indeed be an efficient tool to estimate uncertainties of OA factors, since it is regularly performed to check the stability of factor profiles. Nevertheless, as mentioned earlier, the distribution of factor timeseries from a bootstrap analysis is not available up to now. This will be clearly outlined in the revised manuscript.

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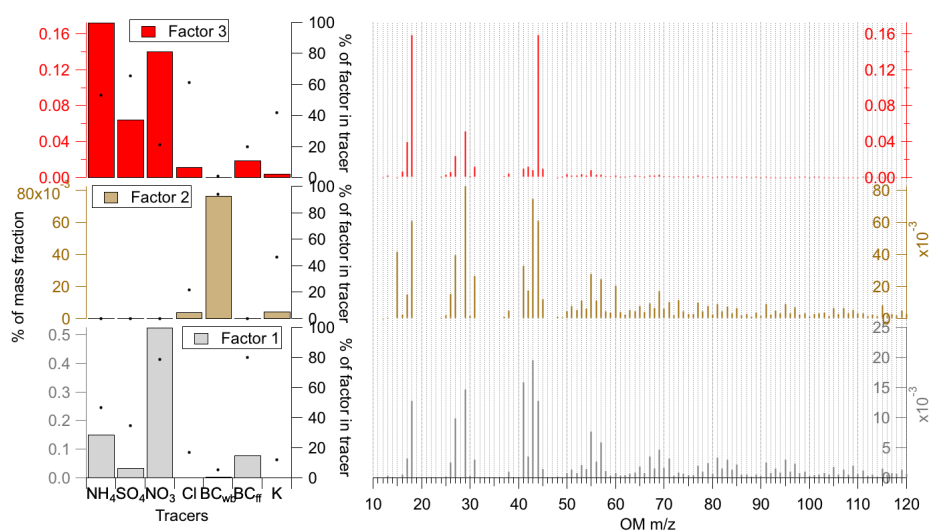


Fig. 1. Figure AC1

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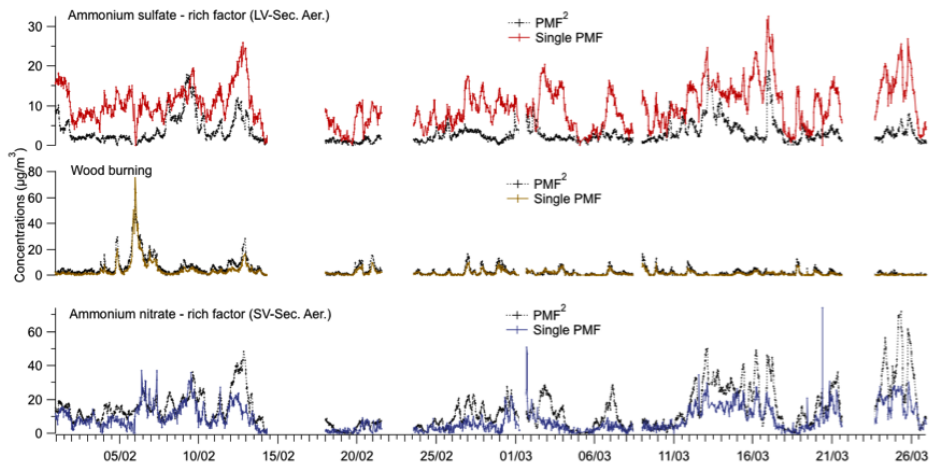


Fig. 2. Figure AC2

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% of bootstrap mapping	Base Factor 1	Base Factor 2	Base Factor 3	Unmapped
Boot Factor 1	97	1	0	2
Boot Factor 2	0	100	0	0
Boot Factor 3	3	1	93	3

Bootstrap mapping of the 3-factor solution

% of bootstrap mapping	Base Factor 1	Base Factor 2	Base Factor 3	Base Factor 4	Unmapped
Boot Factor 1	47	28	16	0	9
Boot Factor 2	3	61	12	0	24
Boot Factor 3	0	0	98	0	2
Boot Factor 4	1	1	3	90	5

Bootstrap mapping of the 4-factor solution

Fig. 3. Figure AC3

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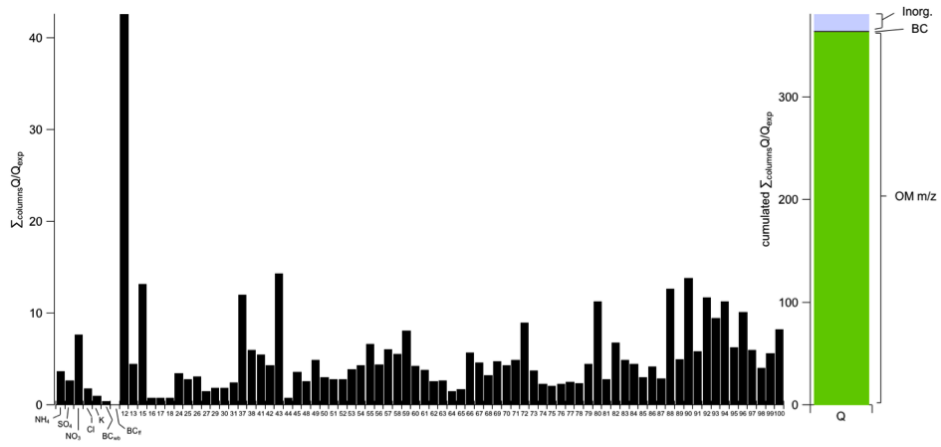


Fig. 4. Figure AC4

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