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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Submicron aerosol source apportionment of wintertime pollution in Paris, France by Double Positive Matrix Factorization (PMF^2) using Aerosol Chemical Speciation Monitor (ACSM) and multi-wavelength Aethalometer" *by* J.-E. Petit et al.

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We first would like to thank Referee#2 for all comments, which are discussed below. The two main comments raised by the review are related to (1) the uncertainty and (2) the benefit of the proposed PMFxPMF methodology.

We fully agree with Referee #2 that "some mixing of source and molecular information

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in PMF factors is inevitable" and that "HOA, p-BBOA, and OOA are far poorly defined parameters"; in fact they feature a certain degree of empiricism in definition. These are part of reasons why the proposed approach represents an attempt to statistically bridge OA factors obtained using a "traditional AMS-PMF methodology" to pollution sources. We see that as a major benefit of our methodology, which cannot be obtained directly via a single PMF analysis including only total OA followed by multi-linear regression analyses.

Similarly to previous studies applying PMF to OA mass spectra, using either "conventional" or "combined" approaches, the present paper does not statistically estimate uncertainties of the obtained factor time-series (in terms of error bars), simply because there is no adequate way to do it up till now. However, the robustness of the presented results has been thoroughly investigated through many sensitivity tests, mainly available in the Supplementary Material. The following lines described the main results of all sensitivity tests:

- Bootstrap analysis on PMF2 outputs showed very satisfying results for the 4-factor solution (Table 2), whereas the adding of a fifth factor leads to a less stable solution (Table B.1). - The choices of a-values for BBOA and HOA reference profiles have been carefully investigated. It appeared that a wide range of a-values (from 0.05 to 0.8) led to very similar results, in terms of timeseries' slopes and r2 (Fig. D1 and D2). Correlation coefficients were always higher than 0.98, while slopes were comprised between 0.7 and 1.1. Highest discrepancies were actually observed when comparing constrained and unconstrained PMF, with slopes going to 1.26 and 1.6 for BBOA and OOA, respectively (Table C.1). The PMFxPMF methodology was thus applied using unconstrained OA factors, and gave very similar factor profiles and timeseries (Fig. C.2). - The determination of the relative uncertainties of OA factors and BC constituents used in the second PMF has been cross-validated, as they appear to respectively contribute to 49% and 31% of total Q/Qexp (Fig. E.1). Within sensitivity tests, these uncertainties have thus been ranged (from 20% to 50%), representing a valuable investigation of the

ACPD
14, C5227–C5231, 2014

weight of these variables in the PM1 source apportionment step. While BC uncertainties don't significantly change final results (Table E.1), the 30-40% uncertainty range for OA factors leads to i) similar profiles and timeseries (with highest discrepancies for the traffic factor, linked to the proportion of ammonium nitrate in the factor profile, Fig E.3), and ii) a wider distribution of OOA in the traffic factor profile (p.14176 l1-13). These pieces of information are distributed here and there in the manuscript and detailed in the Supporting Material. It might be worth gathering them together to better appraise the significance of these results.

We also thank Referee #2 for the technical comments. The following lines are dedicated to our answers to them. 1. Page 14166, Line 5: Would it be an issue that ACSM and Aethalometer have different size-but inlets? A: The size-distribution of Black Carbon is dominated by submicron aggregates. Thus, very little bias are assumed when combining PM2.5 BC and NR-PM1 species. A sentence and references will be added in the manuscript for clarity.

2. Page 14166, Line 18: What is the correlation (r2) between total BC and m/z 60, thus does BC apportionment really improve the correlation? A: The correlation coefficient between (unapportioned) BC and m/z 60 is about 0.23, whereas the correlation between BCwb and m/z 60 is 0.73, strongly suggesting the ability of the Aethalometer model to apportion BC, in addition to the studies using chemical markers, such as levoglucosan.

3. Page 14166, Line 23: Please clarify if the correlation refers to r or r2. A: All correlation coefficients presented in the manuscript refer to r2. We thank Referee #2 for pointing out this imprecision, and the manuscript will be corrected accordingly.

4. Page 14169, Line 11-12: What is the definition of "enough weight"? How can you quantify the weights of different parameters/species? The "weight" of a given variable in PMF analysis can be related to the relative uncertainty used through the Polissar approach. Too low, the considered variable may be explained by only one factor; too

ACPD
14, C5227–C5231, 2014

high, an unspecific distribution of this specie in all factor profiles is likely to occur. Its "weight" can thus be linked to its contribution to Q/Qexp. Appendix E is dedicated to the investigation of the choice of the relative uncertainty for OA factors. A clear link to this appendix will be added in the manuscript.

5. Page 14171, Line 12: 44% and 5.5% of PM1 or PM2.5? A: This refers to PM1. We thank Referee #2 for pointing out this omission, and the manuscript will be corrected accordingly.

6. Page 14172, Line 3-7: Higher ambient temperatures typically move partitioning towards the gas phase, and so the high particulate ammonium nitrate during the third period may not be related to the gas-particle partitioning. A: We thank Referee #2 for highlighting this confusion. The 3rd period is indeed characterized by highest temperatures, and also highest temperature amplitudes during the day. Only the temporal variation of ammonium nitrate (with fast diurnal increases and decreases) is linked to its gas-particle partitioning. This will be corrected in the manuscript.

7. Page 14172, Line 13: Add "designated to HOA, p-BBOA and OOA" after "The three factor solution". A: This will be added accordingly.

8. Page 14175, Line 19: The high correlation between wood burning and OOA seems to indicate that most of the OOA are primary instead of secondary. As combustion itself is a dynamic oxidation process, what is the time scale of conversion for OA to be considered secondary? A: As Referee #2 pointed out, combustion is a complex process, leading to the emission of various types of organic compounds. Laboratory experiments (i.e. Grieshop et al., 2009) show fast secondary organic aerosol formation from wood smoke, few hours (1-2 h) after light exposure. Meteorological conditions in winter (low temperatures), associated with the presence of oxidants in the troposphere, are to be linked with SOA and OPOA formation. It is also interesting to note that the same occur for traffic emissions (i.e. Chirico et al., 2009). Discussion on this point can be added in the manuscript.

ACPD
14, C5227–C5231, 2014

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ACPD

14, C5227–C5231, 2014