Authors' Response to Referee #1

We thank Referee #1 for the careful review and valuable comments on our manuscript. Comments are addressed below.

Anonymous Referee #1
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This is a very well written paper on demonstrating the usefulness of ME2 in better resolving organic factors using new NR-PM2.5 AMS measurements in Beijing and Xian, China. It is often found in unconstrained PMF analysis that the organic factors are not well resolved, with spectral profiles that indicate mixing of the sources. Separation of BBOA and Combustion COA is illustrated and is useful to apportion PAH in these Beijing and Xian datasets. Furthermore, the PM2.5 measurements suggest that contributions of supermicron particles during haze can be significant and hence NR-PM1 may underestimate fine particle concentrations significantly in severe haze. This paper has provided a lot of new novel insights in the analysis of AMS measurements and is suitable for publication in ACP. I just have a few minor questions for the authors to consider.

1. *The spectral profiles of the unconstrained five factor PMF solutions were compared with those of the average of multiple ambient datasets to illustrate the point of the higher than expected contributions in selected m/z peaks. However, these multiple ambient datasets were likely obtained without the use of ME2. What is the basis of using them as a benchmark for discussing the shortcomings of the unconstrained PMF analysis?*

Response: The goal of this analysis is to set for selected m/z peaks an upper threshold beyond which COA and HOA separated by ME-2 will be considered as "unrealistic" or mixed with other sources. Because literature profiles from unconstrained PMF solutions can be mixed with other factors to varying degrees, they provide us with a range of possibly acceptable profiles. Because of this mixing, the resulting range is likely too wide; however, this is beneficial in the current analysis because it prevents us from discarding valid solutions. Solutions that have passed this selection can be considered as possible, but only some of them are selected as the best representation of the data based on other criteria (e.g. diurnals).

2. *The use of eBC/CCOA from the Beijing results for analyzing the Xian results is a good compromise. It may be useful to check if there is literature to discuss the sources of coal used in Xian and Beijing and their neighboring areas.*

Response: In terms of the emission sources, residential coal combustion is expected to dominate over industrial emissions, as the emission factors from industrial burners (with after-treatment control devices) have been found to be two orders of magnitude lower than the emissions from residential burners (Zhang et al., 2008). The coal used in Xi'an and Beijing and their neighboring areas for residential use is a mixture of different coal types (including anthracite and bituminite) from different locations in North China (including coal from different mining regions). Therefore, we consider the eBC/CCOA from Beijing and its neighboring areas a reasonable mean value representative for Northern China, although we understand that the emission profile of different coals could be different.

3. *It is clear that the ME2 yield more reasonable spectral profiles. It is useful to show if ME2 and typical unconstrained PMF yield very different results in the apportionment of the OA factors.*

Response: We thank the reviewer for a very constructive comment. The differences between the PMF and optimized solutions are important, especially in terms of changes in the relative contributions of the different sources. Specifically, COA and HOA are significantly lower in the optimized solution. The paragraph where the unconstrained and constrained solutions are compared has been modified in the revised manuscript to include a comparison between the relative contributions (Fig. S7 added in the supplementary information) and the correlations with externals (modified table S1) for the unconstrained and optimized solutions.

Changes in text:

Compared to the unconstrained solution (average over 10 seeds), the optimized solution (average over all good *a* value combinations) has more genuine factor profiles (Fig. 3), with decreased contributions of *m/z* 60 in the HOA spectra (from 0.009 ± 0.001% to 0.003 ± 0.001%) and of *m/z* 44 in the COA spectra (from 0.069 ± 0.001% to 0.013 ± 0.002%). **In terms of the relative contributions of the different sources to the total OA (Fig. S7), the optimized solution yielded significantly lower COA (7.0 ± 1.1 % vs. 19.9 ± 0.1% in the unconstrained PMF) and HOA (15.1 ± 1.6 % vs. 25.1 ± 0.1% in the unconstrained PMF).** Moreover, σ_{ALL}**, the object function that we seek to minimize,** decreases considerably from 3.3 ± 0.1 in the unconstrained solution to 1.0 ± 0.1 in the optimized solution. In terms of the model mathematical performance, there is only a moderate increase in the residuals in the optimized solution compared to the unconstrained run. Specifically, *Q* normalized by its expected value (*Q*/*Q*exp) (Paatero and Hopke, 2009) increases from 7.5 ± 0.1 in the unconstrained solution to 8.5 ± 0.4 in the optimized solution. The correlations between the OA factors from the optimized solution and its corresponding tracers are presented in Fig. S~~7~~8. ~~and the correlation parameters (R2 and slope) are reported in Table S1.~~**The correlation parameters (R^2 and slope) are reported in Table S1 for the unconstrained and optimized solutions. Compared to the unconstrained solution, the correlations between COA and its marker ($C_6H_{10}O$) are higher in the optimized solution, while the correlations between OOA and NH_4 are slightly lower in this case, especially during the haze events.**

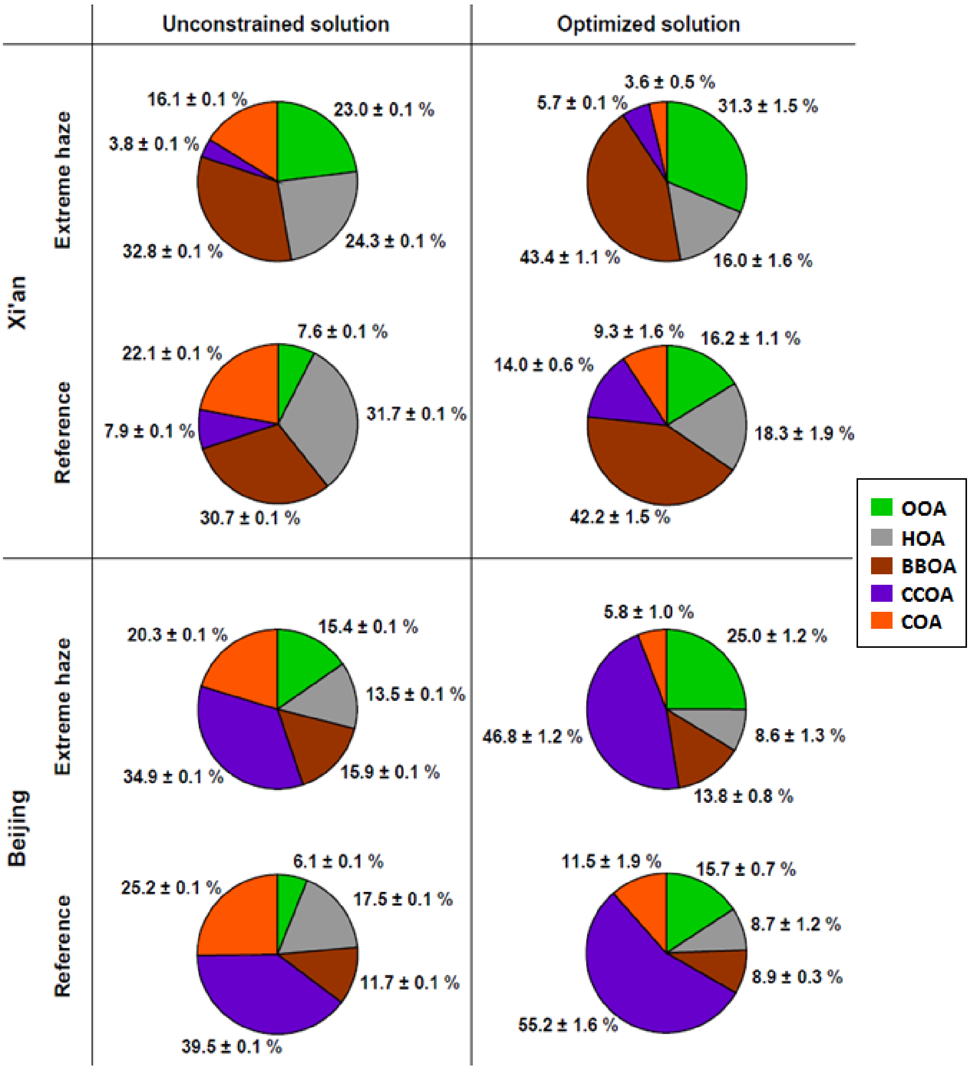

Figure S7 (NEW): **Comparison of the unconstrained and optimized solutions in terms of the relative contributions of the OA sources for the four periods of interest.**

Table S1 (MODIFIED): Squared Pearson coefficient (top) and ratios (bottom) derived from the correlations between the OA sources and its external time series for the four periods of interest as represented in Fig. S7. **The values reported in parenthesis are related to the unconstrained source apportionment solution (average of 10 runs).**

R^2	Xi'an		Beijing		Overall
	Extreme haze	Reference	Extreme haze	Reference	
OOA vs. NH_4	0.22 (0.50)	0.71 (0.83)	0.38 (0.63)	0.60 (0.53)	0.88 (0.92)
COA vs. $C_6H_{10}O$	0.21 (0.008)	0.58 (0.29)	0.44 (0.2)	0.71 (0.53)	0.31 (0.39)
CCOA vs. PAH	0.57 (0.61)	0.59 (0.60)	0.96 (0.97)	0.96 (0.97)	0.62 (0.63)
BBOA vs. $C_2H_4O_2$	0.98 (0.96)	0.96 (0.88)	0.79 (0.80)	0.81 (0.78)	0.97 (0.96)
BBOA vs. eBC_{wb}	0.33 (0.34)	0.53 (0.53)	N.A.	N.A.	0.38 (0.38)
HOA vs. eBC_{tr}	0.61 (0.67)	0.61 (0.62)	N.A.	N.A.	0.61 (0.63)

Ratio	Xi'an		Beijing		Overall
(source/marker)	Extreme haze	Reference	Extreme haze	Reference	
OOA/NH_4	0.99 (0.74)	1.08 (0.64)	0.67 (0.42)	0.76 (0.31)	0.97 (0.70)
COA/$C_6H_{10}O$	60 (219)	144 (267)	126 (372)	198 (304)	96 (243)
CCOA/PAH	3.4 (2.4)	5.5 (3.3)	10.8 (8.4)	10.4 (7.9)	7.2 (5.2)
BBOA/$C_2H_4O_2$	51 (39)	54 (39)	29 (34)	22 (28)	51 (39)
BBOA/eBC_{wb}	10.8 (8.3)	4.9 (3.6)	N.A.	N.A.	7.3 (5.5)
HOA/eBC_{tr}	1.18 (0.62)	1.6 (2.6)	N.A.	N.A.	1.27 (0.63)

4. *Sulfate and OOA can be the result of long range transport after formation elsewhere or local formation. If the former, analysis using local RH may not be that useful. While the OOA does not show any RH dependence, it also has a weak diurnal variation. So, it may not be formed locally.*

Response: This is a good point raised by the reviewer, as we don't have any unambiguous way to demonstrate that the OOA was locally formed. However, during the extreme haze events (with high local RH and high OOA) the wind speed was always close to zero, consistent with very short 72-h back trajectories during this period. This indicates that local and regional emissions (within around 1000 km) are likely very important for the OOA production during such events. The weak diurnal variation may be the result of a significant daytime local OOA production superimposed on a PBL mixing-induced diurnal which would have a minimum during the day (as seen for some of the primary sources).

References:

Zhang, Y., Schauer, J. J., Zhang, Y., Zeng, L., Wie, Y., Liu, Y., and Shao, M.: Characteristics of particulate carbon emissions from real-world chinese coal combustion, Environ. Sci. Technol., 42, 5068–5073, 2008.