



## Supplement of

## New insights into $\rm PM_{2.5}$ chemical composition and sources in two major cities in China during extreme haze events using aerosol mass spectrometry

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1 Table S1: Squared Pearson coefficient (top) and ratios (bottom) between OA sources and its

|                            | Xi'an   |           | Beijing |           | Overall |
|----------------------------|---------|-----------|---------|-----------|---------|
| R <sup>2</sup>             | Extreme | Reference | Extreme | Reference |         |
|                            | haze    |           | haze    |           |         |
| OOA vs. NH <sub>4</sub>    | 0.22    | 0.71      | 0.38    | 0.60      | 0.88    |
| COA vs. $C_6H_{10}O$       | 0.21    | 0.58      | 0.44    | 0.71      | 0.31    |
| CCOA vs. PAH               | 0.57    | 0.59      | 0.96    | 0.96      | 0.62    |
| BBOA vs. $C_2H_4O_2$       | 0.98    | 0.96      | 0.79    | 0.81      | 0.97    |
| BBOA vs. eBC <sub>wb</sub> | 0.33    | 0.53      | N.A.    | N.A.      | 0.38    |
| HOA vs. eBC <sub>tr</sub>  | 0.61    | 0.61      | N.A.    | N.A.      | 0.61    |
|                            |         |           |         |           |         |
| Ratio<br>(source/marker)   | Xi'an   |           | Beijing |           | Overall |
|                            | Extreme | Reference | Extreme | Reference |         |
|                            | haze    |           | haze    |           |         |
| OOA/NH <sub>4</sub>        | 0.99    | 1.08      | 0.67    | 0.76      | 0.97    |
| $COA/C_6H_{10}O$           | 60.21   | 144.01    | 125.54  | 197.79    | 96.35   |
| ССОА/РАН                   | 3.42    | 5.51      | 10.84   | 10.43     | 7.16    |
| $BBOA/C_2H_4O_2$           | 51.02   | 53.98     | 28.75   | 21.68     | 50.60   |
| BBOA/eBC <sub>wb</sub>     | 10.82   | 4.91      | N.A.    | N.A.      | 7.31    |
| HOA/eBC <sub>tr</sub>      | 1.18    | 1.62      | N.A.    | N.A.      | 1.27    |

2 external time series for the four periods of interest as represented in Fig. S7.

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Figure S1. Comparison between mass concentrations obtained from gravimetric measurements of  $PM_{2.5}$  filters (black) and total mass measured with AMS and Aethalometer (blue); Gravimetric analysis only available for the first part of measurements in Xi'an.



Figure S2. (a) Time series of the measured eBC (black) and the eBC calculated (blue) as a linear combination of HOA, BBOA and CCOA for the full measurements period. (b) Correlation between measured and calculated eBC in Xi'an (top) and Beijing (bottom).



Figure S3. (a) PMF profiles for four, five and six factor solution (from left to right); (b) Time
series of the identified profiles for four, five and six factors (from left to right).





2 Figure S4. Relative contribution of m/z 60 in HOA profile over the investigated *a* value space;

3 Acceptable contributions according to Ng et al. (2011) inside red area (mean  $\pm 2\sigma$ ).



5 Figure S5. Averaged COA mass spectra for red cluster (top), blue cluster (center) and purple 6 cluster (bottom) of the three clusters solution shown in Fig. 1. The error bars represent the 7 standard deviation among all solutions in the final *a* value range.

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Figure S6. Investigated *a* value space with color code showing the standard deviation of the
normalized difference between the measured external time series and their fits calculated
using the source apportionment results for: (a) PAH and BBOA, CCOA and HOA; (b) eBC<sub>tr</sub>
and HOA; (c) eBC<sub>wb</sub> and BBOA.



7 Figure S7. Scatter plots between OA sources from the optimized solution and their external

8 tracers; Colors are used to indicate the different periods of interest.



Figure S8. Median diurnal trends for AMS species and eBC during the four periods of
interest. Shaded area represents the 25<sup>th</sup> and 75<sup>th</sup> percentiles (P25 and P75) of the diurnals.





Figure S9. Meteorological parameters during the measurement periods including visibility, wind speed, total radiation, net radiation, dew point, pressure, relative humidity and temperature (from top to bottom); Blue time series were retrieved in situ in the measurement locations and green time series were recorded in nearby local meteorological stations.

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Figure S10. Time series of the OA sources with black shadow representing the standarddeviation among all good *a* value combinations.





Figure S11. Median diurnal trends for OA sources during the four periods of interest. Light
shaded area represents the 25<sup>th</sup> and 75<sup>th</sup> percentiles (P25 and P75) and strong shaded area
represents the standard deviation among all good *a* value combinations.



2 Figure S12. Source regions of the OA sources identified with PSCF analysis for 3 periods of 3 interest (the period with extreme haze in Beijing has too few points for statistically significant 4 PSCF analysis). The color code indicates the normalized cell probability averaged for the 3 5 possible back-trajectory heights (i.e. the probability that a certain pollutant was originated from a certain cell). The marker size is given by a weighting factor that takes into account the 6 7 standard deviation from results at different heights and the back-trajectory counting statistic 8 error. A detailed description of the PSCF methodology can be found in Polissar et al. (1999). 9 The analyses were performed on 72-h wind back-trajectories calculated at 3 different altitudes 10 above the receptor site (i.e. 100, 500, and 1000 m). The backward air mass trajectories were 11 calculated using Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT4; Draxler and Hess, 1998) with a time resolution of 1 hour. Precipitation was taken into account 12 by considering that rain above 0.1 mm h<sup>-1</sup> (Bressi et al., 2014) will result in the wet deposition 13 of the pollutant. An altitude threshold was set to 500 m (sensitivity analyses performed by 14 setting this threshold to 500 m, 1000 m and 1500 m above ground, indicate that the results are 15 not significantly affected by this parameter) and a lower mass threshold corresponding to the 16 75<sup>th</sup> percentile (P75) was used for the mass concentrations (this threshold was tested at P50, 17 P75 and P90; results were found to be similar at P50 and P75, while using P90 did not 18 19 provide statistically robust results).



2 Figure S13: (a) Weighted PAH residuals histogram (blue distribution) and Gaussian fit (black

3 curve); (b) Diurnal variation of weighted PAH residuals.