S.1 Sample collection and sampling sites

The 24-h integrated PM$_{2.5}$ samples were collected on pre-baked (780 °C, 3 h) quartz-fiber filters (8×10 inch) using a high-volume sampler at a flow rate of 1.05 m$^3$ min$^{-1}$. Samples were taken from 5 to 25 January 2013, during the severe haze pollution events, at the urban sites (surrounded by residential areas, without direct emission sources nearby) of Beijing (39.99°N, 116.39°E, 20 m above the ground), Shanghai (31.30°N, 121.50°E, 20 m above the ground), Guangzhou (23.12°N, 113.36°E, 35 m above the ground) and Xi’an (34.23°N, 108.88°E, 10 m above the ground). These four megacities are located in the northern, eastern, southern and western regions of China, respectively.

Beijing, the capital of China, is one of the largest cities in the world and has become a heavily polluted area due to rapid urbanization and industrialization over the past two decades. In 2012, more than 20.7 million residents and 5.2 million vehicles were reported in Beijing (Beijing Municipal Bureau of Statistics, 2013). The national IV emission standard (similar to Euro 4) for new vehicles was implemented on 1 March 2008. Beijing is located in a basin, promoting accumulation of air pollutants and limiting their dispersion. This geographical characteristic, together with multiple emission sources, has led to severe air pollution problems in Beijing.

Shanghai, the largest city by population in China, is a coastal city located at the mouth of the Yangtze River and the centre of the greater Yangtze River Delta metropolitan region, one of the fastest-growing regions in China. In 2012, more than 24 million residents and 2.6 million vehicles were reported in Shanghai (Shanghai Municipal Bureau of Statistics, 2013). The national IV emission standard (similar to Euro 4) for new vehicles was implemented in Shanghai on 1 November 2009.

Guangzhou is the third largest Chinese city and southern China’s largest city. It is located in the Pearl River Delta region and is also one of the fastest-growing regions in China. In 2011, more than 12.7 million residents and 2.3 million vehicles were reported in Guangzhou (Guangzhou Municipal...
Bureau of Statistics, 2012). The national IV emission standard (similar to Euro 4) for new vehicles was implemented in Guangzhou on 1 September 2010.

Xi’an is the largest city in western China, with about 8.6 million residents and 1.6 million vehicles in 2012 (Xi’an Municipal Bureau of Statistics, 2013). The national IV emission standard (similar to Euro 4) for new vehicles was implemented on 1 June 2012. Besides emissions of anthropogenic air pollutants, the city is often influenced by dust particles advected from the Gobi desert. Further, Xi’an is located in the Guanzhong basin, promoting accumulation of air pollutants and limiting their dispersion.

In this study, we collected 21, 14, 11 and 11 PM$_{2.5}$ samples at Xi’an, Beijing, Guangzhou and Shanghai, respectively. At each sampling site, one field blank sample was collected and analyzed following the same approaches used for real samples. The results reported here are corrected for corresponding field blanks. All samples collected were stored at -20 °C until analysis.

**S.2 Chemical analysis**

Table S1 summarizes the measurements taken in this study. Details of each measurement are described in the following subsections. The PM$_{2.5}$ mass on each filter was gravimetrically measured using a temperature and relative humidity controlled microbalance.

**EC/OC and ions.** A 1.0 cm$^2$ punch was taken from each filter for the analysis of elemental carbon (EC) and organic carbon (OC) mass concentrations using the EUSAAR-2 thermal-optical transmission protocol$^{31}$. Replicate analysis shows a good analytical precision with relative standard deviation of 4.8, 9.1 and 5.0% for OC, EC and TC (total carbon), respectively.

Concentrations of water-soluble cations (e.g., K$^+$, Na$^+$, Mg$^{2+}$, Ca$^{2+}$ and NH$_4^+$) and anions (e.g., SO$_4^{2-}$, NO$_3^-$, Cl$^-$, oxalate and methanesulfonate (MSA)) were analyzed using an ion chromatographic system (850 Professional, Metrohm, Switzerland) equipped with a Metrosept C4 cation column and a Metrosept A anion column, respectively, after leaching of a 1.0 cm$^2$ punch of
the filter samples with 50 g of ultrapure water (18.2 MΩ cm) for 30 min at 40°C in an ultrasonic bath.

**Elements.** Elemental concentrations of Fe, Ti, Ca, Zn, As, Pb, Cu and Ni in filter deposits were determined by energy-dispersive x-ray fluorescence (ED-XRF) spectrometry (PANalytical Epsilon 5, Almelo, The Netherlands) and were corrected for field blanks\textsuperscript{32}. Measurement uncertainties were determined as the relative standard deviation of several analyses of the same samples, yielding 7.7% for Fe, 8.6% for Ti, 8.6% for Ca, 7.6% for Zn, 23.5% for As, 7.9% for Pb, 1.7% for Cu and 46.8% for Ni, respectively.

**Organic markers.** Organic marker compounds (see Table S1) were analysed using a recently developed in-situ derivatization thermal desorption gas chromatography time of flight mass spectrometry (IDTD-GC-MS) method. Details of this method are described elsewhere\textsuperscript{14}. Briefly, filter punches were placed into glass liners suitable for an automated thermal desorption unit\textsuperscript{33}. Isotope-labelled standard compounds were spiked onto the filter surface to account for matrix influences for quantification. Derivatization was performed on the filter by adding of liquid derivatization reagent N-methyl-N-trimethylsilyl-trifluoroacetamide (MSTFA, Macherey-Nagel, Germany). During 16 min of desorption time, in addition an in situ derivatization with gaseous MSTFA was carried out to quantitatively silylate polar organic compounds and optimize the desorption process. The derivatization procedure has been automated. Derivatized and desorbed molecules were first trapped on a pre-column before separation by gas chromatography (Agilent 6890 GC, equipped with a BPX-5 capillary column, SGE, Australia). The detection and quantification of compounds was carried out on a Pegasus III time-of-flight mass spectrometer (TOF) using the ChromaTOF software package (LECO, St. Joseph, MI).

The quantified organic markers, listed in Table S1, include 3 anhydrous sugars, 4 lignin breakdown products and 2 resin acids from biomass combustion, 4 hopanes present in lubricant oils in car engines and heavy fossil fuels, such as coal (ref. 34 and references therein), 11 polycyclic aromatic
hydrocarbons (PAHs, including in particular picene, a specific marker for coal burning\textsuperscript{34}) and 8 oxygenated PAHs (o-PAHs).

**Radiocarbon measurement.** Radiocarbon measurements ($^{14}$C) in carbonaceous aerosol were used to quantitatively distinguish fossil and non-fossil sources. Six filter samples (3 high and 3 low PM concentration) were selected from each of the 4 cities (24 samples in total) for $^{14}$C measurements in TC and EC, following the protocol described in Zhang et al.\textsuperscript{15}. These data were then used in conjunction with EC/OC measurements to infer the $^{14}$C content in OC as described below.

A thermo-optical OC/EC analyzer (Model 4L, Sunset Laboratory Inc, USA) equipped with a non-dispersive infrared (NDIR) detector was used for the isolation of different carbon fractions for subsequent $^{14}$C measurements using the four-step thermo-optical protocol Swiss_4S. The method is described in detail in Zhang et al.\textsuperscript{15}. For EC, filter samples were first extracted in water to minimize positive artifacts from OC charring. The water-extracted filter was then heated in 3 steps for OC extraction: step 1 in an oxidizing atmosphere (O$_2$, 99.9995\%) at 375 °C for 150 s; step 2 in O$_2$ at 475 °C for 180 s; step 3 in helium, at 450 °C for 180 s followed by at 650 °C for 180 s. Finally, EC was isolated by the combustion of the remaining carbonaceous material at 760 °C within 150 s in O$_2$. This method is optimized to minimize potential negative EC artifacts stemming from the volatilization of a part of EC during OC extraction steps.

**Table S1:** Offline measurements conducted on the collected filters.

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Method</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM mass</td>
<td>Microbalance</td>
<td></td>
</tr>
<tr>
<td>Ions</td>
<td>IC</td>
<td>Anions: SO$_4$$^{2-}$, NO$_3^-$, Cl$^-$, oxalate and methanesulfonate</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cations: K$^+$, Na$^+$, Mg$^{2+}$, Ca$^{2+}$ and NH$_4^+$</td>
</tr>
<tr>
<td>OC/EC $^{14}$C</td>
<td>Sunset (thermo-optical analyzer) Swiss_4S protocol/MICADAS</td>
<td>EUSAAR-2 protocol in TC and EC. Calculated for OC based on equations 1-3.</td>
</tr>
<tr>
<td>Elements</td>
<td>ED-XRF spectrometry</td>
<td>Fe, Ti, Ca, Zn, As, Pb, Cu and Ni</td>
</tr>
</tbody>
</table>
PAHs: pyrene (PYR), fluorene (FLU), benzo[a]anthracene (BAA), chrysene (CRY), benzo[b]fluoranthene (BF), benzo[a]pyrene (BaP), benzo[e]pyrene (BeP), perylene (PER), dibenz[a,h]anthracene (DAH), indeno(1,2,3-cd)pyrene (IP), benzo[ghi]perylene (BP), picene (PIC).


Resin acids: dehydroabietic acid methylester, dehydroabietic acid.

Anhydrous sugars: galactosan, mannosan, levoglucosan (Lev).

Lignin pyrolysis products: vanillic acid, acetylsyringone, syringylacetone, syringic acid.

Hopanes: 17α(H)-21β(H)norhopane (HP1), 17α(H)-21β(H)hopane (HP2), 17α(H)-21β(H)-22S-homohopane (HP3), 17α(H)-21β(H)-22R-homohopane (HP4).

The EC recovery for $^{14}$C measurement in this work was 78±10%. For the $^{14}$C determination of TC, the filter was combusted in the whole Swiss_4S protocol without OC/EC separations$^{15}$.

After the separation of the desired carbonaceous aerosol fractions (i.e. TC or EC), the resulting CO$_2$ was trapped cryogenically and sealed in glass ampoules for $^{14}$C measurement, conducted with the accelerator mass spectrometer MICADAS using a gas ion source$^{35}$. The $^{14}$C/$^{12}$C ratios in the samples are then related to the isotopic ratio of the reference year 1950 (ref. 36) to determine the fraction of modern carbon in the aerosol ($f_{td}$). Data are then corrected for $^{14}$C decay during the period between 1950 and the year of measurement. Uncertainties of $f_{td(EC)}$ and $f_{td(TC)}$ are <5% and <2%, respectively. The modern fraction in OC, $f_{td(OC)}$, was not directly measured but inferred by
equation 1. By propagating EC/OC and $f_{M}(EC)$ and $f_{M}(TC)$ errors in equation 1, we estimated an $f_{M}(OC)$ uncertainty of ~5%.

$$f_{M}(OC) = \frac{TC \times f_{M}(TC) - EC \times f_{M}(EC)}{OC}$$ (1)

Using $f_{M}(OC)$ and OC mass concentrations determined by Sunset (OC), OC can be divided into two sub-fractions, arising from fossil fuel utilization (OCF) and non-fossil carbon sources (OCNF):

$$OC = OCF + OCNF$$ (2)

$$OCNF = OC \times \frac{f_{M}(OC)}{f_{M}(NF)}$$ (3)

Here, $f_{M}(NF)$ denotes a $^{14}C$ reference value for non-fossil emissions from biogenic and biomass burning emissions, estimated as $1.06 \pm 0.03$ based on a tree growth model described in Mohn et al.\textsuperscript{37} and the contemporary atmospheric CO$_2$ $f_{M}$ (ref. 38).

**Offline AMS.** We applied a novel approach to determine the chemical fingerprint of the bulk organic aerosol, using a high resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS, Aerodyne Research, Inc., Billerica, MA, USA). The method hereafter referred to as offline AMS is fully described in Dällenbach et al.\textsuperscript{39} [Note that the paper was available during review]. Briefly, filter punches were sonicated in 10 mL ultrapure water (18.2 MΩ cm at 25 °C, TOC <3 ppb) for 20 min at 30°C. The water extracts were aerosolized using a custom-made nebulizer. The resulting particles were dried with a silica gel diffusion dryer, and then analyzed by the HR-ToF-AMS. Three types of measurements were performed: (i) filter sample (i.e. collected data); (ii) field blank (blank filter collected at the field site); and (iii) measurement blank (nebulized ultrapure water with no filter extract). The measurement blank was determined before and after every filter sample or field blank. For each measurement, 10 mass spectra were recorded (AMS V-mode, $m/z$ 12-500), with a collection time for each spectrum of 1 minute. The AMS operating principles, calibration procedures, and analysis protocols are described in details elsewhere\textsuperscript{13}. Once per day ultrapure milliQ water was nebulized interposing a particle filter between the nebulizer and the AMS to
provide the gas-phase contribution to the aerosol mass spectrum, which was then subtracted during analysis\textsuperscript{40}. The AMS data were analyzed using SQUIRREL v1.51 (SeQUential Igor data RetRiEvaL) and PIKA (Peak Intergration by Key Analysis) v1.10C, (D. Sueper, University of Colorado, Boulder, CO, USA) for the IGOR Pro software package (Wavemetrics, Inc., Portland, OR, USA). High resolution mass spectral analysis was performed for each $m/z$ in the range from 12-115.

Online AMS measurements provide quantitative mass concentrations of submicron non-refractory aerosol species, including organic aerosol (OA) and ammonium nitrate and sulfate. However, the offline AMS measurements described herein cannot be directly related to ambient concentrations due to uncertainties in filter extraction and nebulization. We account for these uncertainties in two stages. First, the thermo-optical OC measurement is taken as a quantitative measure of the OC mass. This value is multiplied by OM/OC ratios (OM = organic matter) determined from the AMS spectra, yielding ambient AMS OM. AMS HR spectra are then normalized to ambient AMS OM, and these quantitative spectra are subsequently used for source apportionment.

The resulting values cannot be directly used for source apportionment since the AMS-measured species are not extracted and nebulised with equal efficiency. Species-dependent extraction efficiencies (EE) were explored in Dällenbach et al.\textsuperscript{39}, with chemically similar species types approximated by discrete factors obtained by source apportionment analysis. We evaluated EE of hydrocarbon like OA (HOA) from traffic emissions, COA from cooking processes, BBOA from biomass burning and oxygenated OA (OOA), commonly related with secondary organic aerosol to yield $EE_{\text{HOA}}=0.25$, $EE_{\text{COA}}=0.35$, $EE_{\text{BBOA}}=0.78$ and $EE_{\text{OOA}}=0.77$. These values can subsequently be used to extrapolate the source apportionment results to the bulk OA providing quantitative time series of our factors, although this correction induces additional uncertainties (see below).

Compared to the online AMS, the offline AMS technique is subjected to the inherent limitations of filter-based measurements, including sampling artifacts and low time resolution, which hampers the data interpretation (e.g. diurnal variability of certain emissions aerosol sources, such as traffic and
cooking). However, compared to online AMS measurements, the offline technique significantly enhances the spatial coverage of AMS (e.g., 4 cities in this study) and its capability to acquire long-term datasets (1 month in this study); it can be used in combination with other offline measurements (e.g. $^{14}$C and organic markers) for a better characterization of aerosol sources (see below).

**S.3 Source apportionment**

This section describes the methods and results in detail for total PM$_{2.5}$ and OC source apportionment. Two bilinear receptor models were used: chemical mass balance (CMB)$^{11}$ and positive matrix factorization (PMF), with the latter solved using the multi-linear engine (ME-2)$^{12}$. The models are applied to EC/OC, ions and organic marker compounds in addition to AMS data in the case of ME-2. CMB and ME-2 are two complementary approaches and comparing their outputs may be used to tackle their respective limitations. The representativeness of the profiles determined by ME-2 or used in CMB was validated by thoroughly analyzing the residuals’ structure and other environmental parameters (e.g. $^{14}$C measurements and tracer element concentrations). These profiles should be regarded as our best estimates of average source profiles impacting the sites investigated. To the best of our knowledge, this is the first time that such a comprehensive dataset was merged and thoroughly analyzed by multiple approaches to provide the best estimates of PM$_{2.5}$ sources.

Fig. S1 summarizes the apportionment of OC and PM$_{2.5}$ for solutions across all methods (individual methods and their solutions are discussed in detail in the following section.) This comparison illustrates the sensitivity of the source apportionment results to the input data and receptor model algorithms. For the present study, environmentally reasonable solutions agree on average within a factor of two, although the magnitude of the discrepancy between the different apportionments depends strongly on the fraction considered. In this section we discuss the selection of a set of environmentally optimal solutions, while uncertainties in these solutions are discussed in the subsequent section.
Fig. S1. Comparison of average sources contributions to PM$_{2.5}$ and OC estimated by the different receptor models. CMB and ME-2 denote the chemical mass balance and multi-linear engine algorithms, respectively. Several ME-2 solutions are presented and compared. The chemical species presented in Table S2 were considered as input data for ME-2c, whereas for ME-2m, the AMS data were merged with the same species. The subscript numbers beneath ME-2m denote the number of factors selected, from 5 to 9. For ME-2c and CMB, 5 factors are considered, including traffic, biomass burning (BB), coal burning (CB), dust and secondary processes.

S.3.1 CMB

Chemical mass balance (CMB) draws upon source-specific organic markers to assess the contribution of OC emissions from major primary sources. CMB is unable to directly apportion secondary sources, but the fraction of OC not attributed to primary sources considered in the model is regarded as an upper limit estimate for secondary OC (SOC). CMB is based on mass conservation equations, in which known markers’ concentrations ($C_{ik}$) at receptor site $k$ are written as the product of known source profiles $a_{ij}$ and unknown primary source contributions $s_{jk}$ as expressed in equation 4:

$$C_{ik} = \sum_{j=1}^{m} a_{ij} s_{jk} + e$$  \hspace{1cm} (4)
where $m$ denotes the total number of emission sources, $e$ is the residual term minimized in CMB, and $a_{ij}$ represents the fractional abundances of chemical species in the source emissions, expressed as marker-to-OC ratios. Here, the set of linear equations generated by equation 4 is solved with an effective variance weighted least squares method using the Environmental Protection agency EPA-CMB8.2 software. The model requires as input data both measured markers’ concentrations and source profiles together with their associated uncertainties. Uncertainties in the measured markers’ concentrations are estimated based on the analytical technique used, whereas uncertainties on the marker-to-OC ratios in the source profiles are based on their variability across the published profiles (see below). The model outputs are estimates of both source contributions and their respective uncertainties, obtained by propagating the errors of the receptor data and source profiles (entered as input by the operator) through the effective variance least-squares calculations. The magnitudes of the output uncertainties are a function of the input uncertainties and the amount of co-linearity (i.e., degree of similarity) among source profiles.

The main strength of CMB is that, unlike other statistical receptor models, e.g. PMF, it does not require a large dataset and theoretically equation 4 can be solved for an individual sample. Moreover, CMB outputs do not require additional identification of the contributing sources/factors as the profiles are selected a priori for well-defined sources. However, as a result CMB solutions depend strongly on the selection of source profiles, which relies on two implicit assumptions. First, emissions from a given source class are represented by an average source profile with known $a_{ij}$ ratios, which accurately reflects emissions at the receptor site. Second, all the major primary sources of marker compounds and OC (except for secondary OC, as discussed above) are included in the model. Here, we select source profiles representative of Chinese emissions during wintertime (Fig. S2 represents a comparison between combustion profiles used in this study and those available in the literature).

For vehicle emissions (referred to as traffic), we examined two profiles derived from 2 independent tunnel studies conducted at 2 major Chinese cities, Shenzhen$^{41}$ and Guangzhou$^{42}$. The two profiles
compare well and are similar to those reported for other locations\textsuperscript{43}, yielding statistically comparable results when included in the CMB (differences <10\%). For this reason, we have considered an average of the two profiles to represent the traffic emissions in this study.

**Fig. S2.** Comparison of primary source profiles used in CMB for traffic, biomass burning (BB) and coal burning (CB). For traffic, two profiles derived from tunnel studies in China\textsuperscript{41,42} are compared with composite profiles from other tunnel experiments\textsuperscript{43,45} and chassis dynamometer tests of diesel and gasoline cars\textsuperscript{46-48}. For BB the distribution of 33 profiles is displayed\textsuperscript{49-53}. For CB, emission profiles from residential burning of three coal types commonly used in China (anthracite, bituminite, and coal briquettes)\textsuperscript{44} are considered. Specific markers are marked by an asterisk. The markers are explained in Table S1.
For coal burning (CB), we selected a composite profile (the median of three average profiles) of emissions from residential burning of three coal types commonly used in China (anthracite, bituminite, and coal briquettes)\(^44\). While emissions from industrial coal boilers cannot be completely excluded, these are not considered here, as we expect that such processes, due to their high combustion efficiency, contribute little OC. Zhang et al.\(^44\) reported that residential coal burning emission factors exceed by up to 3 orders of magnitudes industrial coal burning emissions, which are characterized by low organic content (OC/PM \~4\% from industrial boilers vs. OC/PM \~40\% from residential stoves). We expect that this profile may satisfactorily represent the OC from coal burning, but most probably lead to an underestimation of the inorganic part of CB emissions.

For biomass burning (denoted BB), we have considered a composite profile of 33 individual profiles for combustion of soft or hardwoods commonly burned in the U.S. and Europe in either residential fireplaces or woodstoves\(^49-53\). The ratios of BB markers to OC considered here (levoglucosan and PAHs, see below) are reasonably stable across published profiles (\(\pm 25\%\); e.g. levoglucosan/OC=0.16\(\pm\)0.03), as these compounds are emitted from both soft and hardwood combustion. By contrast, higher variability in the ratios of these markers to PM and EC is observed (e.g. 0.7<levoglucosan/EC<3.9), because of the high variability of the biomass combustion conditions (a higher burning efficiency tends to decrease the organic fraction in the PM, including levoglucosan). It should be noted that wheat and rice straw burning are common in some parts of China. As these emissions are likely characterized by a lower Lev/OC ratio than used here\(^54\), this may lead to an underestimate of the biomass burning contributions discussed here. However, the fractions of wood and straw burned may vary in time and space, hindering an accurate estimate of the Lev/OC ratio. We therefore expect that the median composite profile considered here, although not pertaining to native Chinese fuels, may be well suitable for the apportionment of BBOC, while less reliable estimates are expected for the BBEC and BBPM. We believe that the approach adopted here (relying on composite profiles representing the median of several individual profiles) gives
statistically more robust apportionments by excluding outlying profiles and down weighting species with variable marker-to-OC ratios.

For dust particles (referred to as dust), we have considered a composite profile of more than 20 source profiles representative of paved and unpaved road dust (ref. 55 and references therein). While the dust elemental composition is consistent across these profiles (e.g. Ca\(^{2+}\)/PM = 0.035±0.005), the fraction of organics therein is widely variable (0.02<OC/PM<0.09). Therefore, we believe that this profile provides reasonable estimates for dust PM, while greater uncertainties are expected for the estimation of dust OC.

In order to assess the contributions from the aforementioned sources, we have selected key markers that are believed to be of low volatility and reasonably stable in the atmosphere under wintertime conditions for use as fitting species. These include levoglucosan (LEV) as a specific marker for biomass burning, elemental carbon (EC) and four of the most prominent hopanes (17α(H),21β(H)-norhopane, 17α(H),21β(H)-hopane, 22S,17α(H), 21β(H)-homohopane and 22R,17α(H), 21β(H)-homohopane, referred to as HP1-HP4, respectively) as markers for vehicular emissions, Ca\(^{2+}\) as a marker for dust and five PAHs (benzo[b,k]fluoranthene, benzo[e]pyrene, indeno[1,2,3-cd]pyrene, benzo[ghi]perylene and picene, referred to as BF, BEP, INP, BP and PIC) from incomplete combustion, in particular coal burning.

Statistical performance measures used as a quality control check of the CMB calculations (see Fig. S3) include the use of R-square (target 0.8–1.0) and chi-square (target 0–4.0) between measured and modelled markers and the absence of cluster sources, i.e. sources with linearly dependent time series\(^1\). Overall, the set of source profiles considered satisfactorily reflects the average measured aerosol at the study sites, as CMB solutions meet the 4 quality control criteria (Fig. S3a). Note that higher residuals are associated with BEP and INP, suggesting some biases between the selected combustion profiles and ambient profiles. In addition, closer inspection of the data shows asymmetric residual distributions, with larger weighted-square-residuals at Xi’an and Guangzhou compared to Shanghai and Beijing (Fig. S3b\(_1\)). This appears to be related to additional
overestimation of BEP levels by the model at Xi’an and Guangzhou (which explains the negative residuals at these two locations, Fig. S3b2) and suggests that a single set of combustion emission profiles is insufficient to simultaneously provide a good representation of the data at all four sites. In the absence of source profiles representative of emissions at the different study sites, we consider that this CMB solution constitutes our best estimate of average source contributions. The comparison of CMB and ME-2 results in section S4 will provide additional measures to evaluate the model performance.

**Fig. S3.** Measures of the statistical performance of CMB, including R-square (target 0.8–1.0), chi-square (target 0–4.0), calculated/measured OC (POC/OC, target<1), measured/calculated markers (M/C, target 1), weighted-residuals time dependant (Σ(M-C)/U) and weighted-squared-residuals (Σ{(M-C)^2/U^2}/df with df=degree of freedom, equal to the number of fitting species minus the number of fitting sources). Overall the model captures the levels and the variability of the markers well. Higher residuals are associated with BeP and INP, suggesting some biases between the combustion profiles selected and ambient profiles. For marker abbreviations see Table S1.

Fig. S4 represents the contribution of different sources to OC estimated by CMB, for the 4 different cities. From these and applying PM\(_{2.5}\)/OC ratios from source profiles, the primary source contributions to PM\(_{2.5}\) are determined. The secondary PM is then determined as the sum of secondary ions (measured \(\text{NH}_4^+, \text{NO}_3^-\) and \(\text{SO}_4^{2-}\) from which the primary part is subtracted) and
SOA, obtained by multiplying secondary OC (OC not apportioned to primary sources by CMB) by an OM/OC ratio of 2 estimated by the high resolution analyses of OA mass spectra acquired from the offline AMS analysis. Good agreement is obtained between measured and calculated PM providing some support to the PM$_{2.5}$/OC ratios from source profiles used.

**Fig. S4.** Source contributions to OC and PM$_{2.5}$, assessed by CMB. Open markers denote measured OC and PM$_{2.5}$ total mass. Results indicate that the model achieves closure supporting to the representativeness of the selected profiles. The secondary fraction dominates OC and PM$_{2.5}$ total mass, while dust constitutes a major fraction of PM$_{2.5}$ in Xi’an.

Overall, these results suggest that CMB reasonably captures the variability and the levels of measured markers and PM$_{2.5}$ concentrations. However, we note that the method is dependent on appropriate *a priori* selection of primary source profiles. Further, it provides only an indirect quantification of the secondary fraction (i.e. as what cannot be explained by known primary sources).
S.3.2 PMF using ME-2

In the PMF receptor modelling technique, both factor profiles and time series are determined within the model. That is, no *a priori* information is required to obtain a mathematical solution. Rather, the output factors are driven by internal correlations between the species contained within the analyzed dataset. This provides great flexibility in the construction of the input data. Important considerations in PMF analysis include the selection of an appropriate number of factors and adequate exploration of the multidimensional solution space, which are discussed in detail below.

In PMF, the data matrix (X) comprising the markers’ time series is expressed as a linear combination of a set of characteristic factor profiles (F) and their time-dependent intensities (G, below the intensities denote the PM$_{2.5}$ mass) such that:

$$ X = GF + E $$

(5)

In the matrix equation (5), E is the residual matrix, defined as the difference between the data matrix (X) and the fitted solution (GF). PMF requires as inputs the data matrix (X) and the associated uncertainty matrix (S). Let $i$ denote the time index, $j$ the species index and $h$ the factors index; $p$ is the total number of factors. Here we solve the equation by the multi-linear engine (ME-2) (ref. 56 and references therein), using the new SoFi interface developed at the Paul Scherrer Institute$^{12}$ within the Igor Pro software package (Wavemetrics, Inc., Portland, OR, USA). The ME-2 implementation of PMF is unique in that it enables complete and efficient exploration of the solution space, including approximate matrix rotations. In contrast, most published PMF analyses are limited in their ability to explore rotational ambiguity in the solution, which can typically only be performed in a single, random dimension. As a consequence, these analyses provide a limited exploration of the solution space, and there is no guarantee that the environmentally optimal solution is even accessible. We implement this rotational exploration in ME-2 by directing the solution towards environmentally-meaningful rotations, through the constraints of a subset of the elements of the factor profile matrix, $F$. The constrained elements of $F$ are set to expected non-
negative anchor values, $f_{h,j}$ (fractional contribution of a marker $j$ to a factor profile $h$), which may vary within a predetermined range defined by the scalar $a (f_{h,j} \pm a \cdot f_{h,j})$. For clarity, we refer herein to this implementation of PMF as “ME-2”, to distinguish it from algorithms with less rotational control.

To calculate the time-dependent contribution from a factor $h$ to a marker $j$ ($t_{sh,j}$), the following equation is applied:

$$t_{sh,j} = g_h \times f_{h,j}$$

(6)

where $g_h$ designates the time-dependent intensity of the factor $h$. To enable a direct comparison between CMB and ME-2, the contribution from a factor $j$ to OC ($OC_h$) is calculated, using a corresponding OM/OC ratio, ($OM/OC)_h$, from high resolution (HR) analysis of AMS mass spectra:

$$OC_h = \frac{OM_h}{(OM/OC)_h} = \frac{g_h \times f_{h,OM}}{(OM/OC)_h}$$

(7)

where $OM_h$ is the time-dependent OM mass ascribed by ME-2 to $h$, calculated as the product of the profile time series $g_h$ and the fraction of OM in the profile $h$.

We have used three different data matrices ($X$) for ME-2:

I. AMS data only (ME-2AMS). Here, the analysis was performed considering the HR organic AMS mass spectra. However, the lack of time-resolved data in our case and the contribution of poorly characterized emissions (e.g. dust) prevented the clear separation and interpretation of the extracted factors. Furthermore, such an approach, despite its widespread use, enables only OA source apportionment, while here we seek identifying the sources of PM$_{2.5}$ and its inorganic/elemental components (e.g. EC, sulfate). Therefore, the ME-2AMS results will not be presented in the following discussion.

II. EC/OC, ions and organic markers (ME-2c, c=chemical), discussed in section S.3.2.1. This approach is commonly applied to offline filter measurements.
III. A merged dataset of the chemical species used as inputs for ME-2c (c=chemical) with AMS organic HR mass spectra (ME-2m, m=merged), discussed in section S.3.2.2.

S.3.2.1 ME-2c

Table S2 shows the measurements considered as input for ME-2c. These include organic species (3 anhydrous sugars, 4 lignin breakdown products, 2 resin acids, 4 hopanes, 11 PAHs and 8 o-PAHs), EC/OC, ions (Cl⁻, NO₃⁻, SO₄²⁻, oxalate, MSA, Na⁺, K⁺, Mg²⁺, Ca²⁺, and NH₄⁺) and residual OM and PM. Residual OM (OMRES) was obtained by subtracting the organic markers concentrations from total OM, calculated by multiplying the measured OC by OM/OC ratios from the HR analysis of the AMS spectra. Residual PM (PMRES) is the difference between total PM₂.₅ mass and the measured species (ions, EC and OM). It represents our best estimate of the particulate chemical species not measured here, most likely dominated by crustal material.

Table S2: $F$ matrix elements constrained in the ME-2/chemical species 5 factors solution. The profiles are normalized to the total PM. The numbers denote the $f_{h,j}$ values constrained in ME-2c, while hyphens denote unconstrained elements.

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Key considerations for ME-2 analysis include the number of factors selected by the user and the constraints on the $F$ matrix elements. Model evaluation is based on the following criteria:

(i) explained variability of the markers by the different factors (Fig. S5);

(ii) comparison of the profiles obtained with published data, especially considering the relative abundances of key markers (e.g. EC and levoglucosan);

(iii) chemical composition of the PM$_{2.5}$ associated with the different sources (Fig. S6);

(iv) comparison between model apportionment of EC sources and those based on $^{14}$C measurements (on average, ~20% of total EC mass originate from non-fossil sources).
We selected a 5-factor solution with some elements of the $F$ matrix elements constrained (see Table S2). To improve the resolution of the minor traffic source, the profile was constrained (with $a=0.5$) to that of He et al.$^{41,42}$. Furthermore, for a clear separation of the biomass burning profile, the contributions of the corresponding markers were set to 0 in all profiles except the BB one (see Table S2). Meanwhile, the hopanes, typically emitted by traffic and coal burning$^{34,57,58}$, were allowed to be allocated by ME-2 only to these 2 sources, by setting their fractional contributions to 0 in all other profiles. The contribution of EC, emitted by combustion sources (traffic, biomass burning and coal burning), was fixed to 0 in non-combustion sources, while it was set to $0.07\pm0.035$ in the biomass burning profile. The latter estimation is based on the ratio between levoglucosan and non-fossil EC, from $^{14}$C analysis. Solutions containing more than 5 factors were then explored (6-10 factors) but could not be successfully interpreted. The 6-factor solution yielded an additional BB profile, probably because of the high variability of biomass burning markers. While this addition clearly decreased the residuals associated with BB markers (by approximately a factor of 1.5), the additional profile was characterized by significant content of calcium and PM$_{RES}$, most likely from dust inputs. This feature is consistent with factor mixing/splitting, an indication for excessive number of factors. Given this lack of improvement in the understanding of the aerosol source apportionment and the mixing between the different profiles, the 5-factor solution was considered as optimal for this setting and therefore discussed in this section.
**Fig. S5.** Fractional contributions of the factors retrieved by ME-2c to the markers.

The chemical fingerprints and contributions of the 5 factors identified by ME-2c are plotted in Fig. S6 and Fig. S7, respectively. While biomass burning and traffic were assessed by constraining some of the elements in their profiles, the other 3 factors were related to coal burning (CB), dust and secondary species, based on the contribution of key markers to their profiles. CB was clearly identified based on the high proportions of PAHs, o-PAHs and hopanes (Fig. S5). The factor profile attributed to dust is characterized by a high contribution of calcium and residual PM (Fig. S5). The latter accounts for 72% of the dust PM$_{2.5}$ mass (Fig. S6) and is most likely composed of crustal material not measured here (e.g. Chow et al.$^{55}$ reported a contribution of Si and Al in dust PM$_{2.5}$ of 27% and 10%, respectively). Explaining most of the variability (60-80% of the total variability) of sulfate, nitrate, ammonium, oxalate and MSA, the last factor was associated with secondary processes (Fig. S5).
Fig. S6. Chemical composition of the PM$_{2.5}$ from different profiles retrieved by ME-2c.

Fig. S7. Source contributions to OC and PM$_{2.5}$, assessed by ME-2c. Open markers denote measured OC and PM$_{2.5}$ total mass. Results indicate that the model achieves mass closure. Compared to CMB, ME-2c apportions a higher fraction of OC to primary sources from combustion processes (biomass and coal burning), while both models suggest the predominance of secondary species in PM$_{2.5}$, especially in Guangzhou and Shanghai.

In general, ME-2c and CMB results are consistent (Fig. S4 and S7): PM$_{2.5}$ factor time series determined by both models are strongly correlated ($R^2 \approx 0.7$). However, ME-2c systematically apportions a higher fraction of OC to primary emissions from biomass and coal burning (+25% for the coal burning OC, +19% for the biomass burning OC) and a significantly lower contribution to secondary PM$_{2.5}$ and OC (-7.5% for secondary PM$_{2.5}$ and -20% for secondary OC). As a result, ME-2c estimates that secondary PM$_{2.5}$ is mainly composed of secondary ions (sulfate, nitrate and ammonium) with relatively lower contribution from secondary OA (SOA) compared to CMB. SOA
from the two models correlate with $R^2=0.52$ (slope=1.8), while a stronger correlation is observed for secondary ions ($R^2=0.83$, slope=1.2). These differences are most prominent at Xi’an and Beijing, while both models consistently predict a very high contribution of secondary species at Guangzhou and Shanghai.

While the obtained ME-2c solution meets the majority of the acceptance criteria and therefore can be considered as a reasonable representation of the data, several observations seem to indicate that the apportionment of the carbonaceous fraction by the model can be further optimized. In particular, ME-2c estimates that ~40% of EC originates from biomass burning, whilst $^{14}$C measurements suggest that this fraction is only ~20%. This underestimate of fossil EC is also reflected by the high OM/EC ratio in the traffic profile estimated to be around 1.5, significantly above values reported at emissions$^{41,42}$ or other ambient sites in China$^{59-62}$: $0.5<\text{OM/EC or OM/BC}<1$, where BC denotes the black carbon. The model also predicts a significant contribution of unidentified species in the BB profile (33% of BB PM$_{2.5}$), while we expect biomass burning aerosol constituents to be quantitatively accessible by the analytical methods applied here (a great part is composed of OC/EC and the rest is ash of which >90% is KCl and K$_2$SO$_4$)$^{63}$. As a result, ME-2c estimates for the (PM/Lev)$_{\text{BB}}$ ratio are 2.7 times higher than those reported in the literature: (PM/Lev)$_{\text{BB}} \sim 10.5$ (ref. 54 and references therein). This is interpreted as stemming from the correlation between biomass burning tracers at Xi’an with dust components, including the unidentified PM$_{2.5}$ fraction and a better separation between the 2 factors may require additional markers.

**S.3.2.2 ME-2m**

To elucidate the differences observed above between CMB and ME-2c, the OA spectral profiles determined by AMS were included in the ME-2 as additional variables (ME-2m). We acknowledge that this approach introduces additional uncertainties and limitations as discussed below, but enhances the explanatory power of the model. This is because AMS data, while not as chemically specific as the measured marker compounds, provide some chemical resolution across the entire
bulk OM. This additional chemical information, when coupled with source-specific marker compounds, provides a more robust apportionment of the OM.

The data matrix for ME-2m was obtained by allocating the OM mass used above as input data to the different OA fragments from AMS. As a result, the new input matrix contains 165 AMS fragments, 46 chemical species and 57 time points (total dimension: 211 data points × 57 time points = 12027 total points). The corresponding uncertainty matrix has the same dimensions. The uncertainties associated with the AMS fragments were calculated and modified following the recommendations of Ulbrich et al.\textsuperscript{64} and Dällenbach et al.\textsuperscript{39}.

When applying ME-2 to data from several sources (in this case, measurement techniques), care must be taken to ensure the solution does not systematically over-/under-represent data from a particular source. The problem arises when, as is frequently the case, variables measured by a particular instrument (e.g. the AMS) are not fully independent. This raises the possibility that the algorithm may emphasize fitting a particular sector of a merged dataset (i.e. data belonging to a particular instrument) while neglecting the others. The resulting solution is not truly representative of the entire merged dataset, but rather weighted towards a particular instrument. To overcome this issue, we utilize the instrument-dependent weighting procedure developed by Slowik et al.\textsuperscript{65} and implemented for ME-2 by Crippa et al.\textsuperscript{66}, thereby ensuring that both AMS and marker measurement data are well represented in the ME-2 solutions. This criterion was evaluated by examining the residual matrices of the respective data types (see Fig. S21), and satisfactory solutions were selected amongst those where the residuals associated with AMS and marker data are symmetrically distributed. Instrument weights are balanced by the application of a scaling value, $C_{\text{markers}}$, to the markers’ elements in the uncertainty matrix ($S_{i,j}$), generating weighted markers errors, $S_{i,j}^*$: where $S_{i,j}^*=S_{i,j}/C_{\text{markers}}$. An unweighted solution corresponds to $C_{\text{markers}}=1$. For $C_{\text{markers}}>1$, more importance is given by the algorithm during the iteration to the markers (by increasing the apparent signal-to-noise), while the opposite effect is produced by $C_{\text{markers}}<1$. 

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**SUPPLEMENTARY INFORMATION**

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ME-2m results were evaluated based on the same four acceptance criteria as those used in the case of ME-2c. An additional fifth criterion is the correlation of OA mass spectra retrieved by the model with those previously reported from ambient and emission data. The same constraints used for ME-2c (see Table S2) were applied for ME-2m. Additional constraints, including the number of factors selected and the anchors \((f_{i,j} = a*f_{i,j})\) used to control matrix rotations will be stated below. The number of factors was first varied in ME-2m, from 5 to 9 (the number of factors selected, \(p\), is indicated as follows: ME-2mp; see section S.3.2.2.1) and the sensitivity of the results to the selected scalars \(a\) and \(C_{markers}\) is then assessed (see section S.3.2.2.2).

While we note that in the case of ME-2m factor-dependent OA extraction efficiencies (EE) affect the final OA source apportionment, these EE do not affect the acceptance criteria for a solution (e.g. spectra profiles, EC apportionment). Therefore the correction for EE is applied only during the sensitivity analysis before the comparison between CMB and ME-2m results (section S.4) and data presented in this section (including Fig. S1) are not corrected for EE.

S.3.2.2.1 Number of factors

ME-2m5:

First, we examined a 5-factor solution (ME-2m5), which can be directly related to the results derived from CMB and ME-2c. Here, we additionally constrained the mass spectral elements for the traffic profile to the HOA mass spectrum from Mohr et al.\(^{67}\), using \(a=0.6\). As discussed in the following, the obtained solution is suboptimal and therefore will not be considered for further analysis. However, further discussion of this solution is helpful in explaining our ME-2m optimization process.
**Fig. S8.** Chemical composition of PM$_{2.5}$ factors determined by ME-2m$_5$.

Fig. S8 shows the chemical composition of factors determined by ME-2m$_5$. While the factors identified by ME-2m$_5$ are related to the same sources as those apportioned by CMB and ME-2c, the addition of OA mass spectra fundamentally alters the source contributions (Fig. S1). This addition causes a significant decrease in the contribution of biomass burning to levels lower than those predicted by CMB (Fig. S4). The BBOA spectral profile from ME-2m$_5$ (Fig. S9) closely resembles those extracted from AMS datasets in previous studies (e.g. ref. 66 and references therein), characterized by the contribution of oxygenated fragments at m/z 29 (CHO$^+$), 60 (C$_2$H$_4$O$_2^+$) and 73 (C$_3$H$_5$O$_2^+$), from the fragmentation of anhydrous sugars. However, ME-2m$_5$ attributes very little OC to biomass burning with respect to the measured levoglucosan levels (e.g. Lev/BBOC $\sim$0.4 from ME-2m$_5$ vs. Lev/BBOC=0.16 reported at emission, see Favez et al.$^{68}$ and references therein).

Therefore this factor does not provide a realistic representation of the composition of primary biomass burning emission (64% of BBPM is attributed to ions, and 40% of EC is apportioned to BB vs. 20% of non-fossil EC).
Another outstanding issue is that ME-2m₅ predicts, like ME-2c, a low contribution from SOA, although the spectral profile of the modeled SOA is consistent with previously reported OOA spectra (OOA: oxygenated organic aerosol, a surrogate for SOA, Fig. S9). Examining the chemical and spectral profiles of dust and coal burning is in this regard revealing, as their contributions to OC and PM₂.₅ predicted by ME-2m₅ are significantly higher than those predicted by CMB and ME-2c. On the one hand, ME-2m₅ estimates that dust is composed of a large fraction of organic matter, higher than previously observed in emission profiles (OC/PM ~0.2 from ME-2m₅ vs. 0.02<OC/PM<0.09 in dust profiles from Chow et al.⁵⁵). On the other hand, the spectral profile of CB aerosol determined by ME-2m₅ contrasts sharply with those available in the literature, with ME-2m₅ clearly overestimating the contribution of oxygenated species in these emissions ($fCO₂^+$=0.21 from ME-2m₅ vs. $fCO₂^+$=0.05-0.27, see Hu et al.⁶⁹). The higher than expected contribution of oxygenated fragments in primary sources mass spectra suggests that ME-2m₅ attributes a part of...
SOA to the primary emissions. This is because oxygenated fragments in SOA, such as CO$_2^+$, only partially correlate with inorganic secondary species, e.g. $R^2=0.55$ for the correlation with sulfate, but instead show some correlation with combustion emission markers, e.g. PAHs and o-PAHs, $R^2=0.76$ for the correlation between CO$_2^+$ and the sum of o-PAHs. This implies that despite the common formation pathways of sulfate and SOA via secondary processes, the source strengths of their precursors are spatially heterogeneous in China. Such a gradient of SOA/sulfate ratios observed at different sites suggests that 2 source profiles are required to accurately represent the secondary aerosol components at all sites by ME-2.

**ME-2m$_6$:**

Based on the discussion above, we introduced a 6th factor (ME-2m$_6$). Here, the contribution of $fCO_2^+$ in the CB mass spectrum was additionally constrained to literature values$^{69}$. ME-2m$_6$ results, illustrated in Figs. S10-S12, highlight quite readily that this solution yields a better representation of the sources spectral and chemical profiles.
Fig. S10. Fractional contributions of the factors retrieved by ME-2m₆ to the markers.

Fig. S11. Chemical composition of PM₂.₅ factors determined by ME-2m₆.
ME-2m\textsubscript{6} captures both the spectral profile and chemical composition of biomass burning aerosol well, suggesting that this source is predominantly composed of organic aerosol (BBOM/BBPM=0.76) and potassium (K\textsuperscript{+}/BBPM=0.05) and accounts for 17\% of the total EC (Fig. S10), consistent with reported emission profiles\textsuperscript{49-53,63} and \textsuperscript{14}C measurements. The model achieves a good separation between coal burning (CB) and aged organic-rich emissions (referred to as Secondary I), decreasing the contribution of CBOC by a factor of \~4 compared to ME-2m\textsubscript{5}. CB explains around 60\% of PAHs and o-PAHs (Fig. S10) and exhibits a spectral profile consistent with literature data, characterized by high proportions of fragments at \textit{m/z} 41, 51, 55 and 67, from unsaturated and aromatic hydrocarbons (Fig. S12). Dust explains nearly the entire variability of Ca\textsuperscript{2+} and PM\textsubscript{RES} (Fig. S10) and contains \~4.5\% Ca\textsuperscript{2+} and \~8\% OC, consistent with values reported in emission profiles\textsuperscript{55}. Our results suggest that organic carbon in dust is characterized by a high oxygen content, dominating the variability of saturated highly oxidized fragments, such as C\textsubscript{3}H\textsubscript{7}O\textsubscript{2}\textsuperscript{+} and C\textsubscript{4}H\textsubscript{9}O\textsubscript{2}\textsuperscript{+} at \textit{m/z} 75.04 and 89.06, respectively, probably related with humus species. While this is to the best of our knowledge the first separation of the dust spectral profile, it should be noted that this profile pertains only to the water soluble fraction of dust and further measurements are needed to better characterize the total dust OM. As expected, in this setting ME-2 is able to extract 2 secondary factors: an inorganic-rich (referred to as Secondary II) and an organic-rich (referred to as Secondary I). Note that this separation, which clearly enhances our ability to assess the contribution of secondary sources, would not be possible without including AMS data in ME-2. Secondary II and secondary I are characterised by similar mass spectral profiles, typical of highly oxygenated organic aerosol (O:C \~0.9), with the former correlating with secondary inorganic species sulfate, nitrate and ammonium (Fig. S13) and the latter with the aggregate primary emissions from traffic, coal combustion, biomass burning and cooking (Fig. S14). An initial multi-linear analysis also suggests that within our errors both fractions equally contribute to fossil and non-fossil secondary organic carbon, which precludes an unambiguous differentiation of their original sources (e.g. biomass burning/biogenic vs. coal burning/traffic). Instead, the two factors display a noteworthy
spatial variability, with the relative contribution of secondary I to total OM being higher at Xi’an and Beijing, probably due to extensive emissions of hydrocarbon precursors from biomass burning and coal combustion for residential heating at these locations in wintertime. (By contrast the Secondary inorganic-rich factor shows homogeneous concentrations across the four sites). In the following discussion, the sum of the 2 factors will be considered as a representation of the secondary fraction.

Fig. S12. Factor OA mass spectra determined by ME-2m6.
Fig. S13. Correlation of Secondary II (inorganic-rich) factor with secondary inorganic species.

Fig. S14. Correlation of secondary I (organic-rich) factor with the aggregate primary urban organic sources.

**ME-2m7 and higher order solutions:**

Here we seek to estimate the contribution from cooking processes, which have been reported as significant aerosol source in urban locations including Chinese cities\(^5\). In ME-2m7, a 7\(^{th}\) factor was introduced to represent these emissions, by constraining the mass spectrum fragments of this profile (with \(a=0.3\)) to the cooking mass spectrum from Mohr et al.\(^6\). We also assumed no hopanes, EC and biomass burning products in the cooking emissions\(^7\). The resulting spectral fingerprint and overall PM\(_{2.5}\) chemical composition of cooking emissions retrieved by ME-2m7 (referred to as cooking influenced (CI) factor, Fig. S15) are consistent with previous emission and ambient measurements\(^6\). This addition has very little effect on the apportionment of the other 6
sources/factors, and the discussion developed above for ME-2m₆ also applies to the ME-2m₇ case (Figs. S16 and S17).

**Fig. S15.** PM₂.₅ chemical composition and OA mass spectrum of cooking emission determined by ME-2m₇.

**Fig. S16.** Fractional contributions of the factors retrieved by ME-2m₇ to the markers.
Fig. S17. Chemical composition of the PM$_{2.5}$ factors determined by ME-2m$_7$.

Fig. S18. Factor OA mass spectra determined by ME-2m$_7$.

The absence of diurnal profiles and specific organic markers for this factor significantly hamper its clear attribution to cooking emissions. In particular, we cannot exclude inputs from primary or
moderately oxygenated secondary urban emissions to this factor, as the latter explains a part of the variability of o-PAHs, emitted or formed from combustion processes. Therefore, this factor should be regarded as a high estimate of the contribution from cooking emissions. The contribution from this factor to PM$_{2.5}$ does not exceed 6% and hence uncertainties underlying its apportionment have little influence on our conclusions (see below). Higher order solutions (ME-2m$_8$ and ME-2m$_9$) using the same settings yielded additional secondary profiles, without significantly modifying the apportionment of primary sources (Fig. S1). As the additional secondary factor could not be related to specific precursors or formation processes, these solutions are not considered further and the results presented in the main text of the paper are based on ME-2m$_6$ and ME-2m$_7$ outputs.

Fig. S19. Source contributions to OC and PM$_{2.5}$, assessed by ME-2m$_7$. Open markers denote measured OC and PM$_{2.5}$ total mass. Results indicate that the model achieves mass closure.
S.3.2.2.2 Residual analysis and sensitivity of ME-2m7 inputs

In this section, we examine the residual distributions and assess the sensitivity of the ME-2m7 outputs to $a$ and $c$ values used as model inputs. Conclusions drawn from this section also apply to the ME-2m6 case.

A mathematically robust ME-2 solution is characterized by centered normally distributed residuals. Fig. S20 shows the ME-2m7 residuals time series for the 4 sites. While slightly negative (positive) residuals are present in the top panel for Shanghai (Guangzhou), the model equally weights the data at the 4 sites (equivalent weighted-squared-residuals at all sites), indicating that overall the set of modeled profiles can satisfactorily represent the measured data (note that by definition, weighted-residuals values between -1 and +1 are within uncertainty). We note that the negative residuals at Shanghai stem from the underestimation of the AMS hydrocarbon-like fragments from traffic because of their low extraction efficiency. This issue will be discussed in the next section.

![Fig. S20. ME-2m7 residuals time series at the 4 sites (Cmarkers=8).](image)

$$\sum_j e_{i,j}/s_{i,j}$$ denotes the time-dependent residuals ($e_{i,j}$) weighted by the uncertainties ($s_{i,j}$) and $$\sum_j \left(e_{i,j}^2/s_{i,j}^2\right)/df$$ the time-dependent weighted-squared-residuals, with $df =$ degree of freedom ($df=j-p$).

A range of $a$ values was explored. For $a < 0.3$ for cooking emissions and $a < 0.6$ for traffic, the $a$-values selected had very little effect on the apportionment (<10%). Higher $a$-values tended to increase the primary emission contributions but exacerbated the comparisons of the sources’ chemical and spectral profiles with those previously reported. Therefore, $a$-values of 0.3 and 0.6 were selected for cooking and for traffic emissions, respectively.
To ensure that both AMS and marker data are well represented in the ME-2m7, we utilized an instrument dependent weighting procedure, performed through the application of the scaling value, $C_{\text{markers}}$. To determine this value we examined the distribution of variables weighted-squared-residuals as a function of $C_{\text{markers}}$ (Fig. S21). Solutions where both AMS and marker data are equally represented were obtained for $C_{\text{markers}}$ values from 6 to 9. Within this range, the choice of $C_{\text{markers}}$ value has a negligible influence on the results and here we present the ME-2m6 and ME-2m7 solutions with $C_{\text{markers}}=8$.

**Fig. S21.** Influence of the $C_{\text{markers}}$ value on the residuals distribution and model outputs. $Q/Q_{\text{exp}}$ denotes the sum of weighted-squared-residuals normalized by the degree of freedom. Lowest residuals corresponds to $C_{\text{markers}} = 8.3$. $M$, $M_{\text{AMS}}$ and $M_{\text{markers}}$ denote the mode of the weighted-squared-residuals normal distribution for all variables, for AMS fragments and for markers, respectively. A minimum $|M_{\text{AMS}}-M_{\text{markers}}|/M$ represents a balanced solution, corresponding to $C_{\text{markers}} = 7.1$. 
S.4  SOA precursors and general uncertainty assessment

The previous section focused on identification and quantification of important sources and processes governing total and organic aerosol mass. These results depend strongly on the uncertainties in the input data and the model parameters. Additionally, one of the most important features revealed by the results above is the apparent high contribution of SOA, whose initial precursors remain at this stage unidentified. In this regard, $^{14}$C measurements may constitute a valuable tool to evaluate the fossil and non-fossil precursors of this fraction. In the following, we propose a framework in which we 1) assess measurement and modeling uncertainties and 2) combine the source contributions estimated by ME-2 with $^{14}$C measurements to identify fossil and non-fossil SOA precursors and estimate their relative contribution and uncertainties related to these estimations. This was achieved using a statistical approach based on a random sampling algorithm (hereafter referred to as pseudo Monte Carlo calculation), first introduced by El Haddad et al.\textsuperscript{72} and later applied by Zotter et al.\textsuperscript{73}.

S.4.1 OA extraction efficiency

Prior to the pseudo Monte Carlo calculation, ME-2 estimates were corrected for biases due to OA extraction efficiency in water, using EE values ($EE_h$ : EE value for a factor $h$) determined in Dällenbach et al.\textsuperscript{39} and following equation 8.

$$OM_h^{EE} = \frac{OM_h \times EE_{bulk}}{EE_h} \text{ where } EE_{bulk} = \sum (OM_j / EE_j)$$

(8)

Here, $OM_h^{EE}$ and $OM_h$ denote the corrected and uncorrected time-dependent OM mass from a factor $j$, respectively and $EE_{bulk}$ represents the time-dependent extraction efficiency of bulk OM.

Time-dependent PM$_{2.5}$ apportionments ($PM_h$) were then corrected for EE ($PM_j^{EE}$) as follows:

$$PM_j^{EE} = PM_j - OM_j + OM_j^{EE}$$

(9)

When applied without any rotational constraints, the ME-2 algorithm is unaffected by $EE_h$.

Following the approach described above, the correction for EE can thus be implemented
subsequently to ME-2, provided that the factors obtained can be assigned to specific fractions with known $EE_j$. In contrast, when rotational constraints are applied using an anchor profile derived from online data, the underlying assumption is that a factor can be well-represented by a single EE, i.e. that the online and offline factor profiles are comparable. While a major assumption, results in Dällenbach et al. suggest that this approach can satisfactorily reproduce results from conventional techniques (e.g. online AMS and aerosol chemical speciation monitor (ACSM)). This signifies that at least for the constrained factors identified (from traffic and cooking emissions), the correction for EE can be applied subsequently to ME-2. This is rendered possible as the elements of the constrained profiles are free to vary within a predetermined range (based on the $a$ values) to accommodate for biases between the fingerprints of $OM_j$ and $OM_j^{EE}$.

For the current setting where additional elements are merged with AMS data, the correct ratios of OA fragments to marker species are governed by the relationship of $EE_j$ to $EE_{bulk}$. Otherwise, ME-2 may fail to explain the levels of both OA fragments and elements (or require additional factors to do so). Here, traffic is the main constrained profile including organic and elemental material (CI is mainly composed of OM and can thus be corrected for EE following equations 8 and 9). As traffic emissions are composed of unburned hydrophobic hydrocarbons, $EE_{traffic}=0.25$ is expected to be lower than $EE_{bulk}$. While the ratio $EE_{traffic}/EE_{bulk}$ can be used to correct the OM content in the traffic input profile, the estimation of $EE_{bulk}$ (e.g. based on CMB results) remains imprecise because of the contribution of factors with unknown $EE_j$, namely dust and CB. Therefore, we considered a non-EE-corrected traffic profile in the ME-2. Results show that the apportionment of EC (the main constituent of traffic emissions) is marginally affected by biases related to EE. EC is well explained by the model (C/M=0.89±0.1) and its apportionment to different combustion emissions ($EC_{traffic}/EC = 0.55-0.79$) is consistent with $^{14}$C measurements and reported source profiles. By contrast, ME-2 systematically overestimates the measured levels of saturated hydrocarbon-like OA fragments, $[C_nH_{2n+1}]^+$, by up to a factor of 2.5. This indicates that the model may underestimate the organic fraction related to traffic emissions and apportionments of this fraction should be considered as...
lower estimates. We assessed the sensitivity of the results to the OM fraction set in the traffic input profile (e.g. by reducing (OM/PM$_{2.5}$)$_{traffic}$ by up to a factor of 3). Results show that reducing (OM/PM$_{2.5}$)$_{traffic}$ decrease the residuals related to the hydrocarbon-like OA fragments, but has a negligible influence (<10%) on the apportionment of EC and OA to the different combustion factors (a slight increase (9%) was observed in the OA fraction in CB emissions). Through the pseudo Monte-Carlo we assess the sensitivity of the results to biases in the relative $EE_j$ (see below).

S.4.2 Estimation of fossil and non-fossil SOA

Using the fossil ($OC_F$) and non-fossil OC ($OC_{NF}$) concentrations from equations 2 and 3, the secondary carbon mass estimated by ME-2 is apportioned into two fractions originating from fossil ($SOC_F$) and non-fossil ($SOC_{NF}$) precursors:

$$SOC_F = OC_F - POC_F = OC_F - \sum_j^{m} \alpha_j POC_j$$  \hspace{1cm} (10)  

$$SOC_{NF} = OC_{NF} - POC_{NF} = OC_{NF} - \sum_j^{m} (1-\alpha_j) POC_j$$  \hspace{1cm} (11)

where $POC_F$ and $POC_{NF}$ are the concentrations of fossil and non-fossil primary OC, respectively. $POC_j$ denotes the OC fraction from a primary source $j$; $\alpha_j$ is an a priori assumed fossil carbon fraction in $POC_j$ (with $\alpha_j \in [0;1]$) and $m$ the total number of primary sources (here, $m=5$). As a result, OC is reapportioned to 7 fractions originating from traffic, cooking (CI), biomass burning (BB), coal burning (CB), dust and fossil ($SOC_F$) and non-fossil ($SOC_{NF}$) secondary sources.

S.4.3 Pseudo-Monte Carlo analysis

The analysis is performed by incorporating the ME-2 estimates in the equations above (1-3 and 6-11) and proceeds as follows:

i. For each of the input parameters a range was assigned, within which these can vary (see Table S3). The criteria on which we based our assessment of these ranges are developed below (section S.4.4).
ii. The parameters were then allowed to randomly vary within the range predetermined in the previous step, using a random sampling algorithm. This approach is to some extent similar to Monte Carlo calculations and allows vast numbers of combinations of input parameters to be computed. A Monte Carlo simulation would involve testing all possible combinations of input parameters, which would be prohibitive in terms of processing time. In contrast, random sampling is much more effective and for our purposes would essentially provide the same results as a full Monte Carlo analysis.

iii. Following the approach described above, 1000 sets of parameters were randomly generated and subsequently used as inputs in equations 1-3 and 6-11. This provided, for each set of parameters, 57 daily contributions from 6 PM sources and from 7 OC sources, or in total: 1000 sets × 57 data point × 13 fractions = 741000 outputs.

iv. The 741000 outputs were finally clustered by site and by fraction and represented in Figs. S24 (for PM2.5) and S25 (for OC), either as absolute (µg m⁻³, panel a) or relative contributions (%), panel b), distributed based on the estimated uncertainties or the total variability, where the day-to-day variation is additionally taken into account.

S.4.4 Uncertainty ranges selection

We note that estimates of output uncertainties from this methodology are a direct consequence of the uncertainty ranges set for the parameters used in the simulation. Table S3 lists our best estimates of the uncertainties and biases affecting the parameters used; their determination is justified in the following.

<p>| Table S3: Ranges [Low, High] of the different parameters entered as inputs to the uncertainty calculation. E* denotes equations 1-3 and 6-11. |
|---|---|---|---|---|
| E* | Parameters | Variables | Low | High |
| 1,2,3 | OCF, OCNF | EC/TC | 0.75×EC/TC | 1.25×EC/TC |
| | | fₘ(TC) | 0.98×fₘ(TC) | 1.02×fₘ(TC) |</p>
<table>
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<tr>
<th>$f_M(\text{EC})$</th>
<th>$0.95 \times f_M(\text{EC})$</th>
<th>$1.05 \times f_M(\text{EC})$</th>
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<tr>
<td>$f_M(\text{NF})$</td>
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<td>1.09</td>
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</table>

<table>
<thead>
<tr>
<th>$G_j$, $OC_j$</th>
<th>$G_j$, $f_{OM,j}$, $(OM/OC)_j$</th>
<th>15 seeds from ME-2m$_6$ and 15 seeds from ME-2m$_7$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$EE_j$</td>
<td>$EE_{Cl}$</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td>$EE_{Secondary}$</td>
<td>0.70</td>
</tr>
<tr>
<td></td>
<td>$EE_{BB}$</td>
<td>0.65</td>
</tr>
<tr>
<td></td>
<td>$EE_{CB}$, $EE_{dust}$</td>
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</tr>
<tr>
<td>$OA_{traffic}$</td>
<td>ME-2m</td>
<td>ME-2c</td>
</tr>
<tr>
<td>$\alpha_j$</td>
<td>$\alpha_{dust}$</td>
<td>0</td>
</tr>
</tbody>
</table>

I. For EC/OC measurements, the range was designed to encompass biases and uncertainties associated with the separation between EC and OC, which is method dependent$^{75}$. We estimated that the uncertainty related with the ratio EC/TC is 25%, based on Zotter et al.$^{73}$ and references therein.

II. The average uncertainty for the discrimination between fossil and non-fossil TC and EC is estimated to be 2% and 5%, respectively.

III. The ratio between the contemporary biomass $^{14}$C level and that in 1950 is estimated to range between 1.03 and 1.09.

IV. Currently there is a clear lack of a widely accepted, unique methodology to assess the uncertainties related with ME-2 (ref. 56). Here, we considered the uncertainties stemming from the selection of the number of factors (6 or 7 factors) and from the influence of the pseudorandom starting-point of the ME-2 algorithm (seed). In practice, the pseudo Monte Carlo algorithm was set to randomly select the inputs of the equations 6-11 amongst 30 ME-2 possible (interpretable) solutions, determined by initializing each of ME-2m$_6$ and ME-2m$_7$ from 15 different seeds. Each of the 30 solutions contains the $G$ matrix of the time-dependent factor contributions to the total PM$_{2.5}$ and the $F$ matrix, from which the $f_{OM}$ and
were used to calculate the factors contributions to OC (equation 7). As we could not clearly attribute the CI factor to cooking emissions, the approach adopted here can be used to estimate the potential impact of the cooking profile on the apportionment of other sources. In Figs. S24 and S25, we display the cooking contribution only for the runs where ME-2m7 is considered.

V. An important consideration in the case of the ME-2m is the correction of the organic fraction for biases derived from the different extraction efficiencies (EE), implemented in equations 8 and 9 (section S.4.1). In Dällenbach et al.39, we estimated EE for several fractions, with \( EE_{\text{HOA}} = 0.25 \), \( EE_{\text{COA}} = 0.35 \), \( EE_{\text{BBOA}} = 0.78 \) and \( EE_{\text{OOA}} = 0.77 \). For CI, BB and secondary OA, these values were used to correct our data. The uncertainties due to our capabilities in determining these values are used in the simulation (Table S3). However, for traffic, as the ratios between the organic fragments and other elements (e.g. EC) are constrained \emph{a priori}, this correction is more challenging. We addressed this issue by examining the comparison between the traffic fraction estimated by ME-2m and that estimated by ME-2c, where the apportionment results are not affected by EE. ME-2m yields as expected the lowest estimate of the traffic OC contribution (6.7% of the total OC), possibly because of the low extraction efficiency of traffic-related hydrophobic species. In contrast, ME-2c yields the highest estimate of the traffic OC (16% of the total OC), exceeding that predicted by all other models including CMB, possibly because of the influence from secondary carbon inputs to this fraction. In the simulation, we considered ME-2m and ME-2c estimates as reasonable bounds for the contribution of traffic OA (Table S2). For dust and CB, EE values could not be determined in Dällenbach et al.39. Examining the chemical composition of coal combustion aerosol in the literature reveals the contribution of both water soluble (e.g. sugar derivatives and carboxylic acids) and insoluble (e.g. linear, cyclic and branched alkanes) compounds44,76. The water solubility of dust/soil organics may be also highly variable77, depending on the nature of humus constituents (i.e.
Fulvic-Humic acid ratio). Therefore, we assumed that $EE_{dust}$ and $EE_{CB}$ range between $EE_{HOA}$ and $EE_{OOA}$, as the latter two fractions are believed to represent the most hydrophobic and hydrophilic fractions of OA, respectively.

VI. Assumptions made in equations 10 and 11 relate to the fossil/non-fossil origin of the primary organic carbon, represented by the parameters $\alpha_j$, with $\alpha_f=1$ referring to an emission source $j$ exclusively of fossil origin. Accordingly, we fixed in the model $\alpha_{CB}=\alpha_{traffic}=1$ and $\alpha_{CF}=\alpha_{BG}=0$. The origin of dust is more uncertain. At Xi’an dust likely originated from deserts in northwest China, consistent with back trajectory analysis (Fig. S22), although fugitive dust from construction sites and unpaved roads could also be important emission sources given the large construction activities at Xi’an16. Thus, a majority of dust at Xi’an is more likely associated with non-fossil carbon. At the other locations, we cannot exclude the contribution from the re-suspension of road dust, which may partially comprise fossil carbon from asphalt concrete and tire wear debris78. In Fig. S23, we have examined, through an initial pseudo Monte-Carlo simulation, the increase of the fraction of unrealistic negative $SOC_F$ estimates as a function of $\alpha_{dust}$. Results show that at a 95% confidence level, $SOC_F$ is positive for $\alpha_{dust}\leq0.35$ (95% of the $SOC_F$ distribution is positive for a fossil carbon contribution to dust below 35%). Based on this analysis we have set the range of $\alpha_{dust}$ between 0 and 0.35.

![Fig. S22](image_url). 24-h back trajectories of air arriving the measurement sites on each measurement day, calculated using the NOAA HYSPLIT model.
**Fig. S23.** Statistically significant negative estimates of fossil SOC normalized to total observations as a function of $\alpha_{dust}$ (statistically significant estimates are defined as those for which SOC$_F$ is higher than the OC$_F$ measurement uncertainties). At a 95% confidence level, SOC$_F$ is positive for $\alpha_{dust}$ $\leq$ 0.35.

**S.4.5 Pseudo Monte-Carlo results**

A great advantage of the approach adopted here is that very unlikely combinations of parameters will represent only a small percentage of the output. The estimated probability distributions (see Fig. S24 and S25) substantially enhance our capability to evaluate the aggregate measurement and model uncertainties related to the different fractions apportioned. Results show that the uncertainties depend on the fraction and the measurement site considered, but in general, OC apportionments are found to have higher uncertainties, as their determination is strongly dependent on the $f_{h,OM}$ and $(OM/OC)_h$ estimated by ME-2 and on the values assumed for EE. Overall, ME-2 and CMB apportionments are also consistent within our errors, providing additional support for our results.

Both ME-2 and CMB predict that traffic contributions are homogeneous across the 4 sites: ~6-9% of PM$_{2.5}$ and ~10% of OC [Note that the absolute contribution from traffic at Xi’an is relatively higher compared to the levels at the other cities studied here, although the total vehicle fleet in
Xi’an is 30-70% lower. This could be attributed to the lag in implementation of more stringent vehicle emission standards at Xi’an as discussed in S.1]. The uncertainties associated with these estimates are around 20% for PM$_{2.5}$ and 35% for OC, except for Beijing where this source is poorly resolved by ME-2 (uncertainties are around 45% for PM$_{2.5}$ and 65% for OC). The estimation of cooking emissions by ME-2 is highly uncertain, ranging from 1-10%, most probably due to the size of our dataset and the lack of time resolved data and specific markers for this source.

ME-2 predicts an appreciable contribution from biomass burning to OC essentially every day, ranging between 10 and 20% (lower contribution to PM$_{2.5}$ of ~6%). The low errors associated with these estimates (~10%) offers a clear identification of the differences between BB contributions at the different sites: BB contributes 11-17% of OC in Beijing and Shanghai vs. 16-23% of OC at Guangzhou and Xi’an. A noteworthy difference between CMB and ME-2 estimation of the biomass burning contribution at Guangzhou should be noted (18% of OC for ME-2 vs. 33% of OC for CMB), with CMB suggesting a 2-fold higher BB contribution at this site. A thorough inspection of the data revealed that this difference can be attributed to the variability in the biomass burning aerosol composition between the different sites. While at Guangzhou a higher fractional contribution can be observed from levoglucosan and its isomers, sole BB markers in CMB, the contribution of other BB products used in ME-2 (i.e. lignin breakdown products and resin acids) is comparable in Xi’an and Guangzhou, yielding more homogeneous estimations. While the reason for such differences remains at this stage unclear, one can argue that the distribution of BB products is strongly influenced by the type of wood burned and by their differential reactivity in the atmosphere, with lignin breakdown products and resin acids being thought to be more reactive than levoglucosan and its isomers$^7$. Because it contains a greater number of markers, including AMS data, ME-2 is expected to better capture the ‘true’ fingerprint of biomass burning aerosol.

ME-2 apportions a higher fraction of PM$_{2.5}$ to coal burning compared to CMB, while a better match between these two models is observed for OC. This is likely because we neglected the contribution from industrial coal combustion in the CMB, which generates inorganic-rich particles. Despite these
differences, our results clearly reveal the importance of coal combustion in Beijing and Xi’an (9-21% of PM$_{2.5}$ mass (or 17-47 µg m$^{-3}$) compared to 3-5% of PM$_{2.5}$ mass (or 2-5 µg m$^{-3}$) in Shanghai and Guangzhou).

Another striking result from this analysis is the large contribution of dust to PM$_{2.5}$ at Xi’an as identified by both ME-2 (46±2.7%) and CMB (50±9%). The contribution of dust-related emissions to OC has larger errors, due to the uncertainties underlying the correction for EE in ME-2 (23±7% and the variability of Ca$^{2+}$/OC ratio in the dust profile considered in CMB (20±8%). For the other locations the dust contribution is significantly lower: <10% of PM$_{2.5}$ and <6% of OC.

The most notable finding in this study is the overwhelming contribution of secondary species at all locations. This is especially the case for Guangzhou and Shanghai, where the contributions of secondary processes are determined with high statistical confidence (errors <10% for PM$_{2.5}$ and ~10% for OC) and account for on average 60% of OC and 75% of PM$_{2.5}$, respectively. Although the absolute concentrations of the secondary fraction at the other two locations are on average higher (10-40 µg m$^{-3}$ secondary OC and 60-170 µg m$^{-3}$ secondary PM$_{2.5}$), lower relative contributions are assessed due to larger inputs from coal combustion emissions in Beijing (secondary species=51% of PM$_{2.5}$) and from dust related emissions in Xi’an (secondary species=35% of OC and 30% of PM$_{2.5}$). Errors associated with the assessments of the secondary fraction burden at Beijing and Xi’an are also considerably higher, i.e. ~10% for PM$_{2.5}$ and ~20% for OC, respectively. This is not unexpected, as the main discrepancies observed between the different model results (CMB, ME-2c and ME-2m) pertain to the capability of the models to split between the primary and secondary fractions at these locations (see discussion above). Nevertheless, such uncertainties do not undermine the main conclusions presented in the paper that secondary species dominate the PM$_{2.5}$ and OC composition or diminish our ability to discern the spatial and temporal variability of this source. For example, in Xi’an we can clearly detect the decrease of secondary species contribution to PM$_{2.5}$ from 45% to 14% during dust events (when the dust contribution increases from 25% to 60%).
Our results also clearly suggest a higher contribution from fossil emissions to SOA production at Shanghai (SOCF=48±6% of SOA) and Beijing (SOCF=59±9% of SOA) compared to the other two sites, where non-fossil SOA dominates (SOCNF=66±8% of SOA at Xi’an and SOCNF=70±7% of SOA at Guangzhou) despite extensive urban emissions. Note that these are the most advanced estimates involving a great number of parameters and still site-to-site differences revealed by this analysis are statistically significant.

It is certainly true that receptor model solutions inherently contain some degree of uncertainty and rotational ambiguity. However, this does not invalidate receptor model results, but rather necessitates a comprehensive investigation of the solution space, analysis of the solution for internal consistency and consistency with external data, and quantification of associated uncertainties. We are convinced that the analysis presented herein represents not only a state-of-the-art source apportionment analysis, but indeed offers several important improvements relative to previously published efforts. The strengths of the current approach (beyond those of conventional source apportionment analyses) are summarized below.

1) The combination of data presented here is unique: to the best of our knowledge, today no dataset combines measurements of molecular markers, trace elements, ions, EC/OC, OA spectra by AMS and the radiocarbon content in EC and OC. The collection of these data required state-of-the-art measurement techniques, some of which were used for the first time here (e.g. offline AMS) or are only performed in a few laboratories worldwide (e.g. 14C in EC and OC separately). The comprehensive set of measurements in the current analysis enhances our capability to constrain PM sources of both primary and secondary origin to a much greater extent than was the case in earlier studies (Note that previous datasets have often been limited to either AMS data or conventional markers and do not include direct radiocarbon constraints of EC sources, see e.g. the review paper by Viana et al.80 or Jimenez et al.10).

2) Source apportionment analyses are conducted using two complementary and widely used receptor models: CMB and PMF. The agreement between these two models provides additional
support for their overall conclusions. Both models are implemented using methods that address key weaknesses in their conventional usage.

- In CMB, we utilize composite profiles representing the median of several individual profiles, in contrast to the usual practice of selecting a single ‘appropriate’ profile. The composite approach provides a more statistically robust model by excluding outlying profiles and down-weighting species with variable marker-to-OC ratios.

- For PMF, we utilize the multilinear engine (ME-2) algorithm (see Paatero and Hopke and references therein), which in contrast to conventional PMF implementations allows full exploration of the rotational ambiguity of a solution. Efficient exploration of this space is achieved by directing the solution towards environmentally-meaningful rotations through constraining a subset of the factor profiles (i.e. from well-defined, well-characterized sources) towards reasonable values (e.g. EC=0 in secondary profiles). This approach has been recently demonstrated to improve solution quality for PMF analysis of aerosol mass spectra, as evidenced by increased correlation of retrieved factor time series with related markers, and is here applied for the first time to the uniquely comprehensive dataset described above.

3) We have explicitly assessed the model uncertainties and the sensitivity of the results to model inputs and measurement uncertainties via pseudo Monte Carlo simulations. These simulations, combined with \(^{14}\)C measurements, also provide an assessment of the fossil and non-fossil fractions of SOA and related uncertainties. Such analysis has been only used on few occasions (see e.g. El Haddad et al.; Zotter et al.), as a unique approach to explicitly evaluate the statistical robustness of model results.

In summary, we believe the source apportionment analysis presented herein is as robust as permitted by the current state of science, and indeed advances the state-of-the-art in several notable ways.
Fig. S24. Source contributions to PM$_{2.5}$ derived from the pseudo Monte Carlo simulation. a) Absolute (µg m$^{-3}$) concentrations clustered by site and by fraction are presented by the boxes and whiskers considering the total variability in the outputs (due to day to day variability and to the uncertainties) and by the grey bars presenting the variability in the estimates due to our uncertainties. The dark grey bars designate the ranges between the 25th and 75th percentiles of the solutions and the light grey bars the 10th and 90th percentile ranges. b) The same apportionments as in (a) are plotted as relative contributions [%]. Solid lines represent the integrated probability distributions taking into account the uncertainties and the day to day variability, from which the different percentiles can be inferred (e.g. the median contribution from a source $i$, corresponds to the contribution at an integrated probability distribution of 0.5). The boxes and whiskers denote the 10th, 25th, 75th and 90th percentiles of the solutions based on the uncertainties related to the measurements, models and assumptions. As a comparison, the CMB estimates and corresponding uncertainties are also shown as open circles.
Fig. S25. Source contributions to OC derived from the pseudo Monte Carlo simulation. a) Absolute (µg m⁻³) concentrations clustered by site and by fraction are presented by the boxes and whiskers considering the total variability in the outputs (due to day to day variability and to the uncertainties) and by the grey bars presenting the variability in the estimates due to our uncertainties. The dark grey bars designate the ranges between the 25th and 75th percentiles of the solutions and the light grey bars the 10th and 90th percentile ranges. b1, b2) The same apportionments as in (a) are plotted as relative contributions [%]. Solid lines represent the integrated probability distributions taking into account uncertainties.
into account the uncertainties and the day to day variability, from which the different percentiles can be inferred (e.g. the median contribution from a source \( i \), corresponds to the contribution at an integrated probability distribution of 0.5). The boxes and whiskers denote the 10\(^{th}\), 25\(^{th}\), 75\(^{th}\) and 90\(^{th}\) percentiles of the solutions, estimated based on the uncertainties related to the measurements, models and assumptions. As a comparison, the CMB estimates and corresponding uncertainties are also shown as open circles.

### S.5 Examination of potentially unidentified sources

To explore if there are unidentified sources contributing to the primary PM, we have additionally examined the aerosol elemental composition, including crustal and anthropogenic elements (i.e., Fe, Ti, Ca, Zn, As, Pb, Cu, V and Ni), using energy-dispersive x-ray fluorescence (ED-XRF) spectrometry\(^{32}\). Within our uncertainties, we show that Ca is almost entirely solubilized, which justifies the use of Ca\(^{2+}\) as a tracer in the CMB simulation. We have also used Fe and Ti as external key markers for dust to validate our apportionments. As shown in Fig. S26, the crustal markers Ca, Fe and Ti not only correlate remarkably well with dust PM, but also their levels are consistent with those expected based on their abundance in the terrestrial crust, giving strong support for the apportionment of dust PM. We find that biomass burning and traffic emissions do not significantly contribute to the measured elements (apart from soluble potassium from biomass burning). A noteworthy result is that Pb and As are dominated by coal burning (Fig. S27). Cu levels during high pollution events are well explained (80%) by the modelled primary sources, dominated by dust (at Xi’an) and coal burning emissions. Note that Pb, As and Cu are well correlated (R >0.7), consistent with their common origins (apart from Xi’an, where a part of Cu, 10-30%, originates from dust). While coal burning in Beijing explains the levels of Zn and Ni (the relative contribution of Ni in coal burning profiles is highly variable which, together with the high XRF measurement uncertainty (~47%) for Ni, prevents its unambiguous apportionment to coal burning), other sources of Zn and Ni cannot be ruled out in other locations. This is especially the case for Xi’an, where ~50% of the measured Zn concentrations could not be assigned to the identified sources, likely because of the large galvanization activities in Xi’an (12 galvanization factories in downtown Xi’an versus 1 galvanization factory in downtown Guangzhou and none in downtown Beijing and Shanghai).

These processes are expected to be associated with little contribution to OA and PM.
**Fig. S26.** Correlation between dust PM and different elements. Red lines show the expected concentrations based on dust profiles (ref. 55 and references therein).

**Fig. S27.** Correlation between the coal burning PM and measured elements. Red lines show the expected concentrations based on coal burning emission profiles81.

While ship emissions may be a source of PM in coastal cities, back trajectory analysis (see Fig. S22) shows that the prevailing air masses are from the north/northwest during our measurement period. This is typical for winter in China because of the influence from the winter East Asian monsoon. Therefore, we do not expect a significant impact from oceanic air masses influenced by shipping emissions. Measurements of shipping emission tracers also support the low contribution of this source. Specifically, vanadium concentrations are $3.1 \pm 1.8 \text{ ng m}^{-3}$ in Guangzhou and $5.9 \pm 2.4 \text{ ng m}^{-3}$ in Beijing.
ng m\(^{-3}\) in Shanghai, which are near or below the instrument detection limit of 5.0 ng m\(^{-3}\); nickel concentrations are 3.7 ± 2.0 ng m\(^{-3}\) in Guangzhou and 8.4 ± 5.1 ng m\(^{-3}\) in Shanghai. These concentrations are significantly lower than previous measurements in Shanghai (average, 15.8 ng m\(^{-3}\) of vanadium and 71.4 ng m\(^{-3}\) of nickel under coastal airflows) by Zhao et al.\(^82\), where ship emissions were estimated to contribute on average 4.2% of 62.6 µg m\(^{-3}\) of PM\(_{2.5}\). Using vanadium as tracer (as in Zhao et al.\(^82\)), ship emissions are estimated to contribute ≤1.1% of PM\(_{2.5}\) (i.e., 1.1% in Shanghai and 0.75% in Guangzhou) in our study.

S.6 Representativeness of the measurement sites

The PM\(_{2.5}\) samples were collected at a single site in each city. These selected sites are considered as reference for the measurement of urban air as shown in the following studies: Wang et al.\(^83\), Han et al.\(^84\), Cao et al.\(^85\) for Xi’an and Beijing sites; Wang et al.\(^86\), Du et al.\(^87\), Tao et al.\(^88\) for Shanghai and Guangzhou. PM\(_{2.5}\) samples have been collected for more than 10 years at the present sites in Beijing and Xi’an and for more than 8 years for Shanghai and Guangzhou, respectively. Here, we further compare measurements performed at Xi’an, during another haze event, in winter 2010, at five different sites including the present site (Fig. S28). Correlation between the levels of the different PM\(_{2.5}\) species at the different sites is evident, indicating that the selected site in Xi’an is representative of the investigated region. Also, note the striking resemblance between the PM\(_{2.5}\) levels and chemical composition between the two haze events in winter 2010 and winter 2013 in Xi’an, suggesting that similar factors, which we identify in this work, control these events.
Fig. S28. Comparison between measurements performed at Xi’an, during another haze event, in winter 2010, at five different sites including the present site. The average PM$_{2.5}$ chemical composition during the two haze events in winter 2010 and winter 2013 are compared.

S.7 Relevance of SOA formation

Our results show that secondary aerosol contributes 30-77% and 44-71% (average for all four cities) of PM$_{2.5}$ and of organic aerosol, respectively, during the campaign period. Interestingly, on average, SOA and SIA were similarly important (SOA/SIA range 0.6-1.4). The significant SOA formation under wintertime conditions is not yet widely recognised. Here we provide further elements from smog chamber experiments performed in our laboratory and from previous measurements in other locations to support the relevance of SOA formation during winter.

Smog chamber experiments of wood burning emissions were performed following the procedures described in Platt et al.$^{89,90}$, but at lower temperature typical of wintertime (-10 °C) in a temperature-
controlled housing. Results from 5 experiments are shown in Fig S29, representing SOA production potential and rates from low temperature aging of modern wood stove emissions.

**Fig. S29.** Aging of biomass burning emissions performed at wintertime temperature (-10 °C) using a novel setup. The SOA/POA ratio is shown as a function of OH exposure (i.e., [OH] × time). SOA$_{\text{max potential}}$/POA is the maximum SOA potential normalized by POA; $k_{\text{OH}}$ is the SOA production rate via OH chemistry. The interquartile range [Q1-Q3] from 5 experiments is represented by the grey area and the OH exposures necessary to produce SOA equal to POA is represented by the red bar (i.e. at OH exposures of 1.6-5.5 × 10$^6$ molecules cm$^{-3}$ h). The SOA$_{\text{max potential}}$/POA represents the asymptotic values reached by Q1 and Q3.

Data are fitted to provide the maximum SOA production potential ($SOA_{\text{max potential}}$) and SOA production rate ($P_{SOA}$) using the following equation:

$$SOA(t) = SOA_{\text{max potential}} \times (1 - \exp(-P_{SOA})t)$$  
where, $SOA_{\text{max potential}} = EF_{pr} \times Y_{SOA}$ \hspace{1cm} (12)

Here, $SOA(t)$ is the SOA evolution with time (t). $SOA_{\text{max potential}}$ is essentially a bulk yield, equal to the precursors emission factor ($EF_{pr}$) times their secondary organic aerosol yield ($Y_{SOA}$). The underlying assumption of this analysis is that $Y_{SOA}$ remains reasonably constant within the concentration ranges investigated in the smog chamber (20-100 μg m$^{-3}$). The analysis also neglects the reactivity of VOCs against other oxidants (e.g. NO$_3$ and O$_3$), a reasonable assumption given the
low concentrations of oxidants other than OH in the chamber (NO$_3$ is photolysed by the lights used to generate OH and O$_3$ concentrations are below 100 ppb), the slow reaction of these oxidants against known precursors (e.g. aromatic VOCs) and the slightly high concentrations of OH kept in the chamber ([OH] $\sim 3 \times 10^6$ molecules cm$^{-3}$). In order to highlight the importance of SOA compared to primary OA, we normalize $SOA(t)$ by the initial, directly-emitted OA mass ($POA$). As $P_{SOA}$ is fundamentally dependent on the decay rates of the precursors against OH ($k_{OH}$) and the available OH ([OH]), the equation above can be written in function of the exposure of the precursors to OH ($OH_{exp}$):

$$\frac{SOA_{max potential}}{POA} = \frac{SOA}{POA} \times (1 - \exp(-k_{OH}[OH]t))$$  \hspace{1cm} (13)

$$\frac{SOA_{max potential}}{POA} = \frac{SOA}{POA} \times (1 - \exp(-k_{OH}OH_{exp}))$$  \hspace{1cm} (14)

The SOA/POA ratios observed in our low temperature aging studies of wood burning emissions (e.g., 0.4-2.8 at the OH exposures of 2-10 $\times 10^6$ molecules cm$^{-3}$ h, see Fig. S29) are consistent with values reported in the literature at higher temperatures. For example, for open biomass burning, Hennigan et al.\textsuperscript{91} found a SOA/POA interquartile range between 0.3 and 1.2 (OH exposure = 3.9-22.8 $\times 10^6$ molecules cm$^{-3}$ h). For biomass burning exhaust from residential burning, Grieshop et al.\textsuperscript{92,93} found SOA/POA ratios between 0.5-1.8 (OH exposure = 2-18 $\times 10^6$ molecules cm$^{-3}$ h), while Heringa et al.\textsuperscript{94} show SOA/POA ratios up to 5.9 after 5-hour aging at unknown OH exposure. It is noted that the POA concentration and the SOA formation may be enhanced by increased partitioning to the particle phase at low temperatures. To the best of our knowledge, the results shown in Fig. S29 are the first demonstration of the rapid and substantial SOA formation from biomass burning emissions at low, wintertime temperature. While such rapid SOA formation at low temperature may seem counterintuitive, our results are in full agreement with the current understanding of gas-phase reaction mechanisms of SOA precursors with OH and their weak dependence on temperature as discussed in the review paper by Atkinson and Arey\textsuperscript{20}. Hydrocarbons
with carbon number $\geq 6$ (relevant to SOA formation) typically have a slight negative Arrhenius temperature dependencies. For example the reaction rate of toluene against OH is estimated to increase by $\sim 10\%$ when the temperature decreases from $25^\circ C$ to below $0^\circ C$. Therefore, under winter conditions, the reaction rate constants of many compounds relevant to SOA formation do not significantly decrease and SOA production is expected to occur at similar OH exposures during winter and summer. From our low temperature smog chamber results, we estimate SOA production rates for biomass burning emissions to $2.5-6.7 \times 10^{-11}$ cm$^3$ molecules$^{-1}$ s$^{-1}$ via OH chemistry. Very similar rates are found for traffic relevant individual SOA precursors, e.g. $k_{OH} = 2.3 \times 10^{-11}$ cm$^3$ molecules$^{-1}$ s$^{-1}$ for m-xylene, $k_{OH} = 3.3 \times 10^{-11}$ cm$^3$ molecules$^{-1}$ s$^{-1}$ for 1,2,4-trimethylbenzene, $k_{OH} = 5.7 \times 10^{-11}$ cm$^3$ molecules$^{-1}$ s$^{-1}$ for 1,3,5-trimethylbenzene$^{20}$, highlighting the rapid reaction of many emissions with OH in the atmosphere. Such rates imply chemical lifetimes against OH of only hours under typical atmospheric conditions.

As shown in Fig. S29, SOA exceeds POA at OH exposure between $1.6-5.5 \times 10^6$ molecules cm$^{-3}$ h for the aging of biomass burning emissions. Rapid SOA formation is also observed from the aging of gasoline vehicle emissions$^{95,96}$, including gasoline cars conforming to the Euro 4 emission standards which are dominant in the cities studied here (see S.1). The question is whether such OH exposures can be reached on a reasonable timescale given wintertime OH concentrations in China.

To estimate OH concentrations in China during the winter haze event of 2013, we now include model data in the form of Geos-Chem benchmark outputs (downloaded from http://ftp.as.harvard.edu/gcgrid/geos-chem/1yr_benchmarks/v9-02/v9-02r/geosfp/Run1/, see Fig. S30), suggesting that monthly average OH concentrations (including daytime and nighttime) are, even in northern China, greater than $0.4 \times 10^6$ molecules cm$^{-3}$. Certainly, the limitation of the Geos-Chem global model used here is the rather coarse resolution, which is partially justified for the very regional characteristic of Chinese haze periods as studied here. Major uncertainties include the extent of primary VOC and NOx emissions and the vertical dilution determining the OH sink but also the emissions and production of OH precursors. This model was used to estimate the lower
tropospheric OH levels at southern California and a good agreement was found with the four years measurements by the Jet Propulsion Laboratory\textsuperscript{97}.

We note that wintertime OH levels were traditionally thought to be low because of the low O\textsubscript{3} levels in China during winter. However, very recent studies from four years of ground-based observations at Beijing and Xianghe (Hebei province, China) show that OH production from HONO photolysis is more than 10 times higher than that from O\textsubscript{3} photolysis in winter\textsuperscript{98}. To our knowledge, no direct measurements of ambient OH radical concentrations in China during winter exist. However, the values estimated here using the Geos-Chem model outputs are consistent with measured wintertime values at polluted urban locations such as Birmingham (UK), Tokyo (Japan), and New York City (median daily maximum 1-2 $\times$ 10\textsuperscript{6} molecules cm\textsuperscript{-3}; mean nighttime concentration 1.5-2.7 $\times$ 10\textsuperscript{5} molecules cm\textsuperscript{-3})\textsuperscript{99-101}.

**Fig. S30.** Simulated monthly averaged OH levels in China during January 2013 from the Geos-Chem model (model version, v9-02r with the latest meteorological data provided by the Global Modeling and Assimilation Office (GMAO) at NASA Goddard Space Flight Center). The model
includes 80 species and > 300 reactions in the troposphere (see Bey et al.\textsuperscript{102}). We are grateful to the Geos-Chem model developers.

Our low temperature smog chamber data (Fig. S29) in combination with the simulated OH concentrations suggest that, considering OH oxidation only (i.e. as a lower limit of oxidative chemistry), SOA exceeds POA in 4-14 hours considering the lowest simulated OH concentration of $0.4 \times 10^6$ molecules cm$^{-3}$ and the OH exposure ranges stated above. This is rapid relative to atmospheric transport during stagnant conditions, providing direct mechanistic evidence that SOA may form rapidly even under wintertime OH concentrations. Note that the average SOA/POA ratios estimated for the four cities during this wintertime haze period are between 0.8 and 2.5. The higher values are found in the south, likely due to higher OH concentrations. Higher values also occur during haze events, probably because of increased stagnation.

While we clearly show that OH oxidation only may explain the observed high SOA during haze events, it should be noted that OH-initiated oxidation is not the only route to SOA formation, other pathways such as NO$_3$-initiated nocturnal chemistry and aqueous-phase chemistry may even be more important. This is certainly the case for secondary inorganic species such as sulfate and nitrate. The aqueous-phase chemistry is likely enhanced during haze events in China, due to the high relative humidity values recorded (on average ~60%, maximum >90% for the entire measurement periods of this study). For example, Sun et al.\textsuperscript{103} showed that high concentrations of secondary aerosol in the haze-fog episodes in wintertime 2004 in Beijing were likely due to the higher sulfur and nitrogen oxidation rates in the aqueous-phase. Wang et al.\textsuperscript{21} also observed high concentration of sulfate and nitrate associated with aqueous-phase reactions during haze events in urban Jinan, China. In this setting, sulfate contributes appreciable amounts (up to 40 % of PM) despite its slow reaction against OH ($k_{OH} = 2 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$) and the low OH levels. Also nitrate, a well-known secondary species, has been observed in winter time in many European and Asian areas, with contributions up to 40% of the total PM\textsuperscript{21,103,104}. When sulfate and nitrate may form via other routes than OH oxidation, so may SOA. For example, Ervens et al.\textsuperscript{22} provide in their
review evidence that this does also apply to organic species even though the magnitude of it is still not very well known. Turpin and co-workers\textsuperscript{105} report that water-soluble organic products of gas-phase photochemistry dissolve into the aqueous phase where they can react further to form low volatility products that are largely retained in the particle phase. Organic acids, oligomers and other products form via radical and non-radical reactions, including hemiacetal formation during droplet evaporation, acid/base catalysis, and reaction of organics with other constituents (e.g., NH$_4^+$). With the current knowledge, it is not possible to predict the relative magnitude of the different processes (OH chemistry vs. aqueous-phase chemistry vs. NO$_3$ chemistry). However, we are able to provide compelling evidence that OH chemistry is sufficient to explain our observations, even though we explicitly do not imply that OH chemistry is the dominant pathway.

References


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