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$PM_{2.5}$ Source Apportionment Using Organic Marker-based CMB Modeling: Influence of Inorganic Markers and Sensitivity to Source Profiles

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ABSTRACT

Chemical mass balance (CMB) is one of the most popular methods to apportion the sources of $PM_{2.5}$. However, the source apportionment results are dependent on the choices of measured chemical species and the source profiles. Here, we explore the sensitivity of CMB results to source profiles by comparing CMB modeling based on organic markers only (OM-CMB) with a combination of organic and inorganic markers (IOM-CMB), using organic and inorganic markers in $PM_{2.5}$ samples collected in the Chinese megacity of Chengdu. OM-CMB results show that gasoline vehicles, diesel vehicles, industrial coal combustion, resuspended dust, biomass burning, cooking, vegetation detritus, SOA, sulphate, and nitrate contributed to 4%, 10%, 15%, 12%, 5%, 3%, 4%, 9%, 10%, and 20%, in comparison to 4%, 11%, 15%, 17%, 6%, 2%, 5%, 10%, 7%, and 18% from IOM-CMB modelling. The temporal variations of $PM_{2.5}$ contributions from sulphate, nitrate, SOA, gasoline vehicles, and biomass burning, characterized by unique markers and low collinearity, were in good agreement between the OM-CMB and IOM-CMB results. However, resuspended dust estimates from OM-CMB had a poor correlation with that from IOM-CMB, due to the different tracers used. When replacing the source profile for industrial coal combustion with that for from residential sources, the contributions of resuspended dust and residential coal combustion were overestimated because the residential coal combustion profile contained a higher concentration of OC and organic compounds but lower crustal elements. Different source profiles for gasoline vehicles were also evaluated. Our results confirm the superiority of combining inorganic and organic tracers and using up-to-date locally-relevant source profiles in source apportionment of PM.

Keywords: particulate matter, source apportionment, CMB model, organic marker

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1. INTRODUCTION

Atmospheric fine particles ($PM_{2.5}$) have long been shown to have pronounced effects on human health (Bell et al., 2014; Yang et al., 2019; Hong et al.,2021; Li et al., 2022; Wen et al., 2022). $PM_{2.5}$ control is a challenging problem, especially in megacities where large populations are exposed to high concentrations. The information on the impacting sources can play an important role in designing effective $PM_{2.5}$ reduction strategies. Many studies have estimated the potential source contributions to $PM_{2.5}$ in megacities using various methods, such as receptor models (Lu et al., 2018; Wang et al., 2013; Perrone et al., 2012; Mor et al., 2021; Song et al., 2021; Zhang et al., 2021a), and air quality models (Clappier et al., 2015; Zhang et al., 2017; Li et al., 2020a; Guan et al., 2021). Among the receptor models, the chemical mass balance (CMB) model approach has been used for source apportionment of PM at many locations, worldwide (Zheng et al., 2002; Perrone et al., 2012; Yin et al., 2015; Chen et al.,2015; Lu et al., 2018; Wu et al., 2020; Wong et al., 2021). This model has some underlying challenges posed by possible collinearity of source profiles, and relevance of source profiles.

$PM_{2.5}$ is comprised of a complex mixture of chemical components, including both inorganic and organic components. As a significant constituent of $PM_{2.5}$, organic matter (OM) is comprised of thousands of compounds which show distinctive physical and chemical properties (Zhang et al., 2013; Zhao et al., 2013; Li et al., 2020b; Cao et al., 2021; Li et al., 2021). Generally, the OM is composed of primary organic matter (POM) which is directly emitted, and secondary organic matter (SOM) which is formed through the chemical oxidation of volatile organic compounds (VOCs) (Yang et al., 2016; Zhan et al., 2021; Zhang et al., 2021b). Numerous studies on $PM_{2.5}$ source apportionment have been conducted based upon inorganic markers and OC (Olson et al., 2008; Li et al., 2020c). However,

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many important $PM_{2.5}$ emission sources (such as cooking) do not have a unique composition (Zhao et al., 2015). Some organic compounds are more specific to individual PM sources and have been used as molecular markers in source apportionment models (Marmur et al., 2006; Schauer and Cass, 2000; Schauer et al., 1996; Robinson et al., 2006; Chow et al., 2007; Arhami et al., 2018; Esmaeilirad et al., 2020; Tian et al., 2021a; Mancilla et al., 2021). An organic molecular marker-based chemical mass balance (OM-CMB) method has been widely used to quantify source contributions to carbonaceous aerosols. The OM-CMB method performs well in the source apportionment of OC, but does not directly estimate contributions of inorganic secondary ions when apportioning $PM_{2.5}$ sources (Ke et al., 2008). Thus, it is advantageous to explore the influence of using both inorganic and organic markers in the CMB modeling of $PM_{2.5}$.

Several studies have applied the OM-CMB model for source apportionment of PM in China (Zheng et al., 2005; Liu et al., 2016; Guo et al., 2013; Wang et al., 2009; Wu et al., 2020; Xu et al., 2021). However, the organic source profiles they used were mainly derived from measurements made in the United States, which may be less representative of the local sources and current conditions of the sources in China.

Therefore, this paper aims at exploring the influence of introducing inorganic markers, and the sensitivity to source profiles. $PM_{2.5}$ source apportionment was conducted by CMB modeling based on organic markers (OM-CMB) and by a combination of organic and inorganic markers (IOM-CMB). Commonly used markers (including OC, EC, ions, elements) and organic markers (including polycyclic aromatic hydrocarbons (PAHs), n-alkanes, hopanes, levoglucosan, palmitic acid, stearic acid, and cholesterol) in $PM_{2.5}$ collected in a Chinese megacity were analysed. Source apportionment

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of OC was conducted by the OM-CMB approach, and then the other source contributions to $PM_{2.5}$ were indirectly estimated. In addition, source apportionment of $PM_{2.5}$ was directly conducted by the IOM-CMB method, and source contributions to $PM_{2.5}$ estimated by the OM-CMB and the IOM-CMB methods were compared. In addition, the sensitivity to different source profiles for coal combustion and gasoline vehicles were tested.

2 METHODS AND MATERIALS

2.1 Sampling

$PM_{2.5}$ samples were collected from a megacity in China, Chengdu (102°54' to 104°53' E, 30°05' to 31°26' N), from January to December in 2018. The city is located in Southwestern China with a population of more than 14 million. As the capital of Sichuan province, Chengdu is a centre of economic development and transportation in Southwestern China, with continuous development of industry and changes in traffic conditions (Shi et al., 2015; Liu et al., 2015).

The sampling site is at the Environmental Protection Building (EPB, 104°04′ E, 30°35′ N), which is located in a mixed residential and commercial area of the downtown city (Shi et al., 2017). There is no obvious industrial emission near the building. The sampling points are located on the rooftop of the EPB building, which is approximately 25 m above ground level. Daily samples were collected and each sampling lasted for 22 h. The sampling was stopped during rainy days. There were 64 $PM_{2.5}$ samples collected during the whole year, involving spring (March, April and May), summer (June, July and August), autumn (September, October and November), and winter (January, February and December). The dry season (Jan. to Apr., Dec.) and wet season (Jun. to Oct.) were both well represented.

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The samples were collected using two medium-volume air samplers (TH-150, Wuhan Tianhong, China) with a flow rate of 100 L/min. Polypropylene (90 mm in diameter) and quartz filters (90 mm in diameter) were used to collect particulate matter. After sampling, the quartz filters were kept in aluminum foil bags and stored at −4 °C.

2.2 Chemical analysis and quality assurance and quality control (QA/QC)

The following source tracer components were analysed: OC, EC, ions, elements, PAHs, n-alkanes, hopane, levoglucosan, fatty acids, and cholesterol. The particles collected on the polypropylene filters were used for the analysis of elements including Si, Ca, Al by inductively coupled plasma-mass spectrometry (ICP-AES) (IRIS Intrepid II, Thermo Electron). A 1/4 section of each filter was placed into an acid solution (HNO_3: HCl: H_2O_2 = 1: 3: 1). The quartz filters were used for the analysis of the water-soluble ions (NH_4^+, Cl^-, NO_3^- and SO_4^{2-}) and carbon fractions (OC and EC). A 1/8 portion of each filter was cut and placed in a centrifuge tube with 8 ml of distilled deionized water and the solutions were refrigerated for 24 hours, filtered and analyzed with a Thermo ICS900 Ion Chromatograph (Thermo Electron) (Tian et al., 2013). Carbon components were measured by a thermal/optical carbon aerosol analyzer (DRI 2001A, Atmoslytic Inc.) based on the IMPROVE thermal/optical reflectance (TOR) protocol.

Organic compounds, including 11 n-alkanes, 17 PAHs, 3 hopanes, 2 fatty acids, levoglucosan and cholesterol, were measured by gas chromatography-mass spectrometry (GC-MS). The full names and corresponding abbreviations of the components are summarized in Table 1.

A 1/4 of each quartz filter was cut and put into a tube prior to analysis of PAHs, n-alkanes, and hopane.

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It underwent a sonicated extraction with 20 mL dichloromethane and n-hexane (v/v 1:1) under ice bath conditions twice, each for 15 min, and filtration into a round-bottomed flask by a 0.22 μm filter. After passage through a pre-activated solid phase extraction cartridge and elution with n-hexane, the solution was concentrated under reduced pressure on a rotary evaporator to near dryness (less than 5 ml). Finally, the volume was reduced to 1 ml after a slow nitrogen blow. The internal standards (naphthalene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12, and perylene-d12; hexamethylbenzene; n-tetracosane-d50) were added to the samples and the samples were stored at under -4 ℃ in darkness until analysis (Liu et al., 2015).

Another 1/4 of the quartz filters was cut and put into tubes to analyze fatty acids and cholesterol. Fifteen ml methanol and 10 ml dichloromethane (v/v 1:2) were added into the tubes and sonicated, then extracted for 10 min 3 times. The solution was filtered into a round-bottomed flask using a 0.22 um filter. After concentration by a rotary evaporator to near 5 ml, the solution was concentrated to 1 ml by a high purity nitrogen gas stream. The extract was derivatized by BSTFA plus 1% TMCS at 70 ℃ for 2 h, and used for analyzing the concentrations of n-alkanoic acids and cholesterol (He et al., 2006; Schauer et al., 1999). The internal standard (hexamethylbenzene) was added to the samples. The last 1/4 of the quartz filters was cut and put into a tube to analyze levoglucosan through a high-performance anion-exchange chromatography with pulsed amperometric detection (HPAEC-PAD) (Herisau, Switzerland) with a Hamilton RCX-30 250 column.

The other organic markers were analyzed by GC-MS (7890B/5977B, Agilent, USA） using a 30m × 0.25 mm diameter DB-5MS capillary column (0.25μm film thickness). The carrier gas was pure helium (purity of 99.99% or more) at a constant flow rate of 1.0 mL min^{-1}. For PAHs and hopanes,

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157 inlet and transfer line temperatures were set to 230℃ and 280℃ respectively. For n-alkane analysis,
158 inlet and transfer line temperatures were set to 300℃. EI mode was used and the ionization energy
159 level was 70eV.
160
161 Quality assurance and control were highly valued throughout the whole experiment. All samples and
162 blank filters were analyzed using the same methods. Quartz filters were baked in an oven before use
163 to remove organic interference. Before and after sampling, all the filters were equilibrated at the same
164 environmental condition for 48 h in desiccators before weighing. Each filter was weighted by a
165 sensitive microbalance with balance sensitivity ±0.010 mg.
166
167 Field and laboratory blanks were measured to correct the corresponding data. The same procedure
168 was used to analyze standards every day, including standards for each n-alkane, PAHs mixture, each
169 hopane (O2Si Smart Solutions, USA); standards for PALMIA, STEARA, and CHOL (Dr.
170 Ehrenstorfer, Germany); and standard for LEVOG (U.S. Pharmacopeia, USA). The recovery values
171 of all target components showed a low relative standard deviation. In addition, the first sample of
172 every ten samples was re-examined and the precision was found to be within 10%. The recoveries
173 were 79-106% for elements, and 96-110% for ions. For carbon fractions, a system stability test (three-
174 peak detection) is required before and after detecting samples and the relative standard deviation
175 should not exceed 5%. The recoveries of most organic compounds ranged from 60%-130%.
176
177 In addition, the chemical species were reconstructed using the following equations referred to in the
178 IMPROVE Report V (Hand et al., 2011):
179

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Ammonium sulphate = $1.375[SO_4^{2-}]$ (1)

Ammonium nitrate = $1.29[NO_3^-]$ (2)

Organic matter (OM)=1.8[OC] (3)

Crustal material =2.2[Al]+ 2.49[Si]+1.63[Ca]+2.42[Fe]+1.94[Ti] (4)

Other = PM-sulphate-nitrate-organic matter-crustal material-EC (5)

2.3 Chemical Mass Balance (CMB) Modelling

The CMB model has been used extensively as a receptor model in air pollution source apportionment studies. The model is mainly based on two assumptions: 1) The measured chemical and physical properties must present in different proportions in different source emissions, and 2) the changes in these proportions are negligible or can be approximated during the process of particulate matter transport from the source to the receptor (Watson et al., 2002). Two methods were used to conduct the source apportionment of $PM_{2.5}$. The organic marker-based CMB (OM-CMB) model was used in this study to apportion the sources of OC and $PM_{2.5}$ (Schauer et al., 1996; Villalobos et al., 2017). This model was applied to determine the primary source contributions (including gasoline vehicles, diesel vehicles, industrial coal combustion, resuspended dust, biomass burning, cooking, and vegetation detritus) to OC, and the contributions of the primary emission sources to $PM_{2.5}$ were calculated using the ratios of $PM_{2.5}$ mass to fine OC in each source. The SO_4^{2-} and NO_3^- were not included in the OM-CMB modeling, but they were measured in the profiles of above primary sources, so the contributions of secondary SO_4^{2-} and NO_3^- were calculated by the difference between the measured concentrations and the amount estimated in the primary source emissions (Zheng et al., 2002), and then they were converted to ammonium sulphate and ammonium nitrate using the equations (1) and (2) above. In addition, the secondary organic carbon (SOC) was considered as the

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unresolved source, and was calculated as the difference between measured OC and the sum of all significant contributions to OC (Villalobos et al., 2017).

For the inorganic and organic marker-based CMB (IOM-CMB) model, $PM_{2.5}$ source apportionment was conducted based on inorganic and organic source profiles as showed in Table 1. The profiles of gasoline vehicles, diesel vehicles, industrial coal combustion, resuspended dust, biomass burning, cooking, soil dust, sulphate, and nitrate were inputted into the CMB model, and their contributions were directly obtained. The SOC was also calculated as the difference between measured OC and the sum of all primary contributions to OC, and then was converted to SOA through equation (3). The other difference from the OM-CMB is that the source profiles of vegetation detritus did not work in this calculation, and a soil dust profile was used. Although they are two different source categories, their profiles are similarly characterized by high loadings of C31 and C33 n-alkanes (Tian et al., 2021b) due to vegetation influence. Details of the source profiles used in the two methods will be discussed in Section 2.4. The components introduced into the OM-CMB and IOM-CMB are summarized in Table 1.

To ensure the reliability of the fitting results, the following parameters were used to evaluate the model outputs of the two methods. The percent mass explained by the model is typically between 80 and 120%. For goodness-of-fit parameters, high r^2 (>0.8) and low χ^2 (<4) were required. In addition, the MPIN (modified pseudo inverse normalized) matrix was checked to determine the marker of each source category.

In addition, an independent estimation of the SOA was also conducted by the EC tracer method

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(defined as the SOA_{EC}) to compare with the SOA estimated the OM-CMB and IOM-CMB. Assuming EC totally comes from primary sources and the OC/EC ratio in primary sources is relatively constant, SOC_{EC} was estimated as in Turpin and Huntzicker (1995):

$$SOC_{EC} = OC - EC*(OC/EC)_{pri} \quad (6)$$

$$SOA_{EC} = 1.8[SOC_{EC}] \quad (7)$$

where OC and EC are the measured ambient concentrations; $(OC/EC)_{pri}$ is the OC/EC ratio in primary aerosols. $(OC/EC)_{pri}$ values of 2.0-2.2 are usually applied to identify and estimate SOA (Xu et al., 2021). In this study, the lowest OC/EC ratio of all samples was observed as 2.0, so $(OC/EC)_{pri}=2.0$ was used.

2.4 Source Profiles

The source profiles applied in this study include: (1) gasoline vehicles, diesel vehicles, coal combustion, resuspended dust and soil dust which were measured by ourselves (Tian et al., 2021b); (2) biomass burning (Wang et al., 2009; Pirovano et al., 2010), cooking (Zhao et al., 2015), and vegetative detritus (Rogge et al., 1993; Hildemann et al., 1991) from other publications; and (3) ammonium sulfate and ammonium nitrate which were used to represent secondary sulphate and nitrate. To test the sensitivity of CMB results to source profiles, two different profiles of coal combustion (residential vs. industrial coal combustion as in Tian et al., 2021b) and seven different profiles of gasoline vehicles (as in Tian et al. (2021b) vs. those from U.S. noncatalyst vehicles in Schauer et al. (2002) and from Chinese gasoline vehicles in Cai et al. (2017) were evaluated for CMB modelling. Inorganic ions and elements were not showed in the Cai et al. (2017), so only OM-CMB

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249 can be compared.

250

251 **3. RESULTS AND DISCUSSION**

252 **3.1 $PM_{2.5}$ Chemical Composition**

253 The daily concentrations of the $PM_{2.5}$ and mass closure of main species are shown in Figure 1a. $PM_{2.5}$
254 concentrations ranged from 28 to 237 μg m^{-3}. For the mass closure of $PM_{2.5}$ chemical composition
255 referred to the equations (1) to (5), the fractions were in the order of OM (29%) > nitrate (24%) >
256 crustal material (23%) > sulphate (15%) > EC (5%). The daily mass closures were generally
257 consistent with the daily $PM_{2.5}$ concentrations.

258

259 The daily concentrations of organic components are shown in Figure 1b to 1e. Their concentrations
260 were in the order of $\sum_{10}$n-alkanes (99-393 ng m^{-3}) > levoglucosan (16-894 ng m^{-3}) > ∑unsaturated
261 fatty acids and cholesterol (29-157 ng m^{-3}) > $\sum_{14}$PAHs (1-96 ng m^{-3}) > $\sum_{3}$hopanes (1-31 ng m^{-3}).
262 The concentrations of n-alkanes, levoglucosan, PAHs and hopanes showed similar temporal
263 variations with $PM_{2.5}$ concentrations, while unsaturated fatty acids and cholesterol showed different
264 variations.

265

266 **3.2 Source Contributions to OC**

267 The annual average of the source contributions to OC estimated by the OM-CMB is shown in Figure
268 2a. The highest contributor for OC was SOC (34%), followed by biomass burning (17%), diesel
269 vehicles (10%), industrial coal combustion (9%), gasoline vehicles (8%), resuspended dust (8%),
270 vegetation detritus (8%), and cooking (6%).

271

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The daily percentage contributions to OC are shown in Figure 3a. The highest daily contributions to OC reached 6 μg m^{-3} for gasoline vehicles, 4 μg m^{-3} for diesel vehicles, 3 μg m^{-3} for industrial coal combustion, 4 μg m^{-3} for resuspended dust, 8 μg m^{-3} for biomass burning, 2 μg m^{-3} for cooking, 3 μg m^{-3} for vegetation detritus, and 14 μg m^{-3} for SOC. The percentage contributions of gasoline vehicles were higher during January when the $PM_{2.5}$ concentrations were the highest (due to a heavy pollution episode). The percentage contributions of industrial coal combustion were higher during the dry season. The biomass burning showed higher fractions during autumn and winter. The high vegetation detritus concentrations were mainly observed during spring (April). The higher SOA fractions were observed during August to October when photochemistry is most active and primary emissions of some components are lower. The contributions of diesel vehicles, resuspended dust, and cooking showed no obvious seasonal variation.

3.3 Source Contributions to $PM_{2.5}$

As described in the methods section, for the OM-CMB model, the source contributions to $PM_{2.5}$ were converted from the contributions to OC. The average source contributions and conversion ratios are summarized in Table S1. For the IOM-CMB model, the source contributions to $PM_{2.5}$ were directly estimated. Figures 2b and 2c describe the annual average source contributions to $PM_{2.5}$. The percentage contributions of gasoline vehicles, diesel vehicles, industrial coal combustion, resuspended dust, biomass burning, cooking, vegetation detritus, SOA, sulphate, and nitrate were 4%, 10%, 15%, 12%, 5%, 3%, 4%, 9%, 10%, and 20% for OM-CMB, and 4%, 11%, 15%, 17%, 6%, 2%, 5%, 10%, 7%, and 18% for IOM-CMB.

The daily percentage contributions to $PM_{2.5}$ estimated by the two methods are shown in Figures 3b

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and 3c, and the absolute contributions are shown in Figure 4. The highest daily contributions to $PM_{2.5}$ reached 21 and 20 μg m^{-3} for gasoline vehicles, 28 and 24 μg m^{-3} for diesel vehicles, 33 and 39 μg m^{-3} for industrial coal combustion, 34 and 34 μg m^{-3} for resuspended dust, 17 and 17 μg m^{-3} for biomass burning, 6 and 6 μg m^{-3} for cooking, 8 and 8 μg m^{-3} for vegetation detritus, 26 and 25 μg m^{-3} for SOA, 28 and 21 μg m^{-3} for sulphate, and 75 and 66 μg m^{-3} for nitrate, estimated by the OM-CMB and IOM-CMB models, respectively.

As shown in Figure 3b, 3c and 4, the temporal variations of source contributions to $PM_{2.5}$ were similar to those to OC. The gasoline vehicles showed obvious higher contributions during the cold period. Studies have shown that gasoline vehicles emit more PM under poor combustion conditions, such as cold starts at low temperature (Schauer et al., 1999 and 2003). The percentage contributions of industrial coal combustion were higher during the dry season. Hydropower supplies a large percentage of Chengdu's electricity demand during the wet season, while coal combustion is needed for electricity generation during the dry season (Shi et al., 2016). Biomass burning showed higher fractions during autumn and winter, due to residential use and local straw burning activities. A high vegetation detritus/soil dust contribution was mainly observed during spring, while the resuspended dust showed weaker seasonal variations. The vegetation detritus and soil dust are natural sources, and their contributions are associated respectively with vegetation and meteorological condition. The resuspended dust can be caused by high wind strength and intensive human activities (such as road dust caused by heavy traffic, construction dust caused by building activities, etc.).

The highest percentage contributions of SOA and sulphate were observed during August to October. Their formation is associated with photochemical processes which are more efficient because of

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318 strong illumination, less precipitation and high temperature during August to October. The SOA and
319 sulphate also showed higher contributions during January. Although photochemical reactions may be
320 generally weak during January, high precursor concentrations, humidity and PM during winter may
321 enhance the aqueous phase and heterogeneous reactions. The highest fraction of nitrate occurred
322 when the temperature was low (as shown in Figure 1). Although photochemical reactions are
323 favourable in summer, nitrate may decompose at higher temperatures due to the thermodynamic
324 instability of ammonium nitrate (Hasheminassab et al., 2014), and the high relative humidity during
325 wintertime in Chengdu can enhance the secondary formation of nitrate through heterogeneous
326 reactions (Liu et al., 2019).
327
328 **3.4 Comparisons of Daily Source Contributions and markers**
329 In this study, except for the soil dust and vegetation detritus, similar source categories were shared by
330 the OM-CMB and IOM-CMB. Thus, a comparison of the contributions estimated by the two CMB
331 methods was conducted. Furthermore, the contributions were also compared with the corresponding
332 markers which had high MPIN values. The temporal variations of source contributions and
333 corresponding markers which had high MPIN were compared, as shown in Figure 4.
334
335 It can be seen that the average contributions of sulphate and nitrate from the OM-CMB were higher
336 than those from the IOM-CMB (as shown in Figure 2), while their daily contributions were highly
337 consistent with each other and with the trends of corresponding markers. The sulfate and nitrate
338 sources from the OM-CMB are the measured values after subtracting the summed mass of sulfate and
339 nitrate emitted from the selected primary sources as described in the section 2.3, while those from the
340 IOM-CMB were directly estimated by the CMB model. The consistent temporal variations of

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contributions indicate they were well estimated by the two methods due to the low collinearity. The difference of average contributions might be caused by uncertainties in the estimation of primary source contributions (such as in resuspended dust), if the actual source compositions differs from the profiles used in the model. As shown in Figure 4, the average values and temporal variations of the SOA from two methods were also in agreement with each other, and with the SOA_{EC} which was independently estimated by the EC tracer method according to equations (6) to (7). The SOA estimated by the IOM-CMB was more consistent with the SOA_{min} than that estimated by the OM-CMB, because EC was used in the IOM-CMB.

According to Figure 2, among the primary source categories, the average contributions of the gasoline vehicles, diesel vehicles, industrial coal combustion and cooking estimated by the two methods were generally consistent, and the average contributions of resuspended dust and dust/vegetation detritus showed larger differences for the two methods. What's more, as shown in Figure 4, the daily variability of biomass burning and gasoline vehicles from two methods showed more consistent temporal variations (with squared correlation coefficient R^2=0.87 and 0.86) than other primary sources (with R^2 ranged from 0.53 to 0.67). The biomass burning and gasoline vehicle contributions also showed similar temporal variations with their corresponding markers. The marker of gasoline vehicles was BghiP and the marker of biomass burning was LEVOG, which were very different from other sources, so their low collinearity with other sources can explain the consistent results. The daily contributions of diesel vehicles and industrial coal combustion of the two methods were moderately consistent. Consistent markers were identified for these two sources by the OM-CMB and IOM-CMB; however, the collinearity between source profiles of diesel vehicles and industrial coal combustion may cause some differences. For example, they are both characterized by high loadings of C24, C25

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364 alkanes and medium-ring PAHs (Tian et al., 2021b). The contributions of resuspended dust estimated
365 by the two methods showed differences, probably because different markers (C31 for OM-CMB and
366 Ca for IOM-CMB) were identified for CMB modeling. Cooking contributions estimated by the two
367 methods also showed weak correlations with each other and with the corresponding marker, which
368 may be due to its contributions being generally low and influenced by other source categories. The
369 STEARA also exists in the source profiles of other sources, so the differences of other source
370 contributions can influence its attribution and the cooking contribution.
371
372 **3.5 Sensitivity of Source Apportionment to Source Profiles**
373 Two different profiles for two major sources - coal combustion and gasoline vehicles - were used to
374 test the sensitivity to source profiles as mentioned above. The result of the IOM-CMB which used the
375 residential coal combustion instead of industrial coal combustion profile is shown in Figure S1.
376 Compared with the result for the industrial coal combustion, the contributions of resuspended dust
377 and residential coal combustion were higher, and the contributions of other sources were lower. The
378 difference between two coal combustion profiles was that the residential coal combustion showed
379 higher OC and organic compounds and lower crustal elements than the industrial coal combustion
380 (Tian et al., 2021b). The lower crustal elements in the residential coal combustion may explain the
381 overestimation of the resuspended dust, whose markers were mainly crustal elements, when using its
382 profile. Residential coal combustion is an important source category in northern China, but there is
383 little in the central city of southern China. Thus, the industrial coal combustion source profile was
384 selected in this study.
385
386 For the gasoline vehicle profiles, most results did not meet the goodness-of-fit criteria when using the

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noncatalyst vehicle profile measured by Schauer et al. (2002). Figure S2 describes the OC-CMB results using the Chinese gasoline vehicle profiles measured by Cai et al. (2017). Except for the heavy gasoline 2, most results were comparable with the results using our gasoline vehicle profiles. In summary, it is important to use local and up-to-date source profiles for the source apportionment, and to include more components in the profiles.

4 CONCLUSIONS

To explore the influence of introducing inorganic markers and sensitivity to source profiles, a comprehensive comparison of $PM_{2.5}$ source apportionment using organic marker-based OM-CMB as well as organic and inorganic marker-based IOM-CMB was conducted. The percentage contributions of gasoline vehicles, diesel vehicles, industrial coal combustion, resuspended dust, biomass burning, cooking, vegetation detritus, SOA, sulphate, and nitrate were 4%, 10%, 15%, 12%, 5%, 3%, 4%, 9%, 10%, and 20% for OM-CMB, and 4%, 11%, 15%, 17%, 6%, 2%, 5%, 10%, 7%, and 18% for IOM-CMB. The temporal variations of $PM_{2.5}$ contributions from sulphate, nitrate, SOA, gasoline vehicles, and biomass burning were in good agreement between the OM-CMB and IOM-CMB results. The OM-CMB and IOM-CMB are powerful to apportion sources characterized by unique markers (such as biomass combustion) and low collinearity. The diesel vehicle and industrial coal combustion estimates were moderately consistent between the two methods. The OM-CMB resuspended dust and cooking estimates showed poor correlation with the IOM-CMB results. The discrepancy in resuspended dust between OM-CMB and IOM-CMB may be due to the different tracers in their source profiles. In addition, when testing the sensitivity to source profiles for two coal combustion and two gasoline vehicle profiles, it was found important to use current and relevant source profiles according to local source information for the source apportionment.

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DATA ACCESSIBILITY

Data supporting this publication are openly available from the UBIRA eData repository at (https://doi.org/10.25500/edata.bham.00000745

AUTHOR CONTRIBUTIONS

YZ and RMH conceived the study. YZ, RMH, and ZS guided the work and wrote the paper. XW and PZ carried out the chemical analysis and data analysis.

COMPETING INTERESTS

The authors declare that they have no conflict of interest.

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TABLE CAPTION

Table 1: Full names and abbreviations of the components used in the OM-CMB and IOM-CMB.

FIGURE CAPTIONS

Figure 1: The daily concentrations of $PM_{2.5}$, mass closure of main species, and organic components. (a) Mass closure of main species; (b) n-alkanes; (c) PAHs; (d) hopanes; (e) unsaturated fatty acids and cholesterol.

Figure 2: (a) The average of percentage contributions to OC estimated by the OM-CMB; (b) The annual average of percentage contributions to $PM_{2.5}$ estimated by the OM-CMB; (c) The annual average of percentage contributions to $PM_{2.5}$ estimated by the IOM-CMB; (d) Comparison of contributions to $PM_{2.5}$ estimated by the OM-CMB and IOM-CMB.

Figure 3: (a) Daily contributions to OC estimated by the OM-CMB; (b) Daily contributions to $PM_{2.5}$ estimated by the OM-CMB; (c) Daily contributions to $PM_{2.5}$ estimated by the IOM-CMB.

Figure 4: Comparisons among source contributions estimated by the OM-CMB and IOM-CMB, and corresponding markers.

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729 **Table 1.** Full names and abbreviations of the components used in the OM-CMB and IOM-CMB.
730

Components	Abbreviations	Used in OM-CMB	Used in IOM-CMB
organic carbon	OC		Yes
element carbon	EC		Yes
ammonium	NH_4^+		Yes
chloride	Cl^-		Yes
nitrate	NO_3^-		Yes
sulfate	SO_4^{2-}		Yes
aluminum	Al		Yes
silicon	Si		Yes
calcium	Ca		Yes
polycyclic aromatic hydrocarbons	PAHs		
phenanthrene	Phe	Yes	Yes
anthracene	Ant	Yes	Yes
fluoranthene	Flt	Yes	Yes
pyrene	Pyr	Yes	Yes
benz(a)anthracene	BaA	Yes	Yes
chrysene	Chr	Yes	Yes
benzo(b)fluoranthene	BbF	Yes	Yes
benzo(k)fluoranthene	BkF	Yes	Yes
benzo(e)pyrene	BeP	Yes	Yes
benzo(a)pyrene	BaP	Yes	Yes
dibenz(a,h)anthracene	DBA	Yes	Yes
Indeno(1,2,3-cd)pyrene	IPY	Yes	Yes
benzo(ghi)perylene	BghiP	Yes	Yes
coronene	Cor	Yes	Yes
hopanes			
17α(H)-22,29,30-Trisnorhopane	C27a	Yes	Yes
17α(H),21β(H)-30-Norhopane	C29ab	Yes	Yes
17α(H),21β(H)-hopane	C30ab	Yes	Yes
n-alkanes			
n-tetracosane	C24	Yes	Yes
n-pentacosane	C25	Yes	Yes
n-hexacosane	C26	Yes	Yes
n-heptacosane	C27	Yes	Yes
n-octacosane	C28	Yes	Yes
n-nonacosane	C29	Yes	Yes
n-Triacontane	C30	Yes	Yes
n-hentriacontane	C31	Yes	Yes
n-dotriacontane	C32	Yes	Yes
n-tritriacontane	C33	Yes	Yes

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Others			
levoglucosan	LEVOG	Yes	Yes
palmitic acid	PALMIA	Yes	Yes
stearic acid	STEARA	Yes	Yes
cholesterol	CHOL	Yes	Yes

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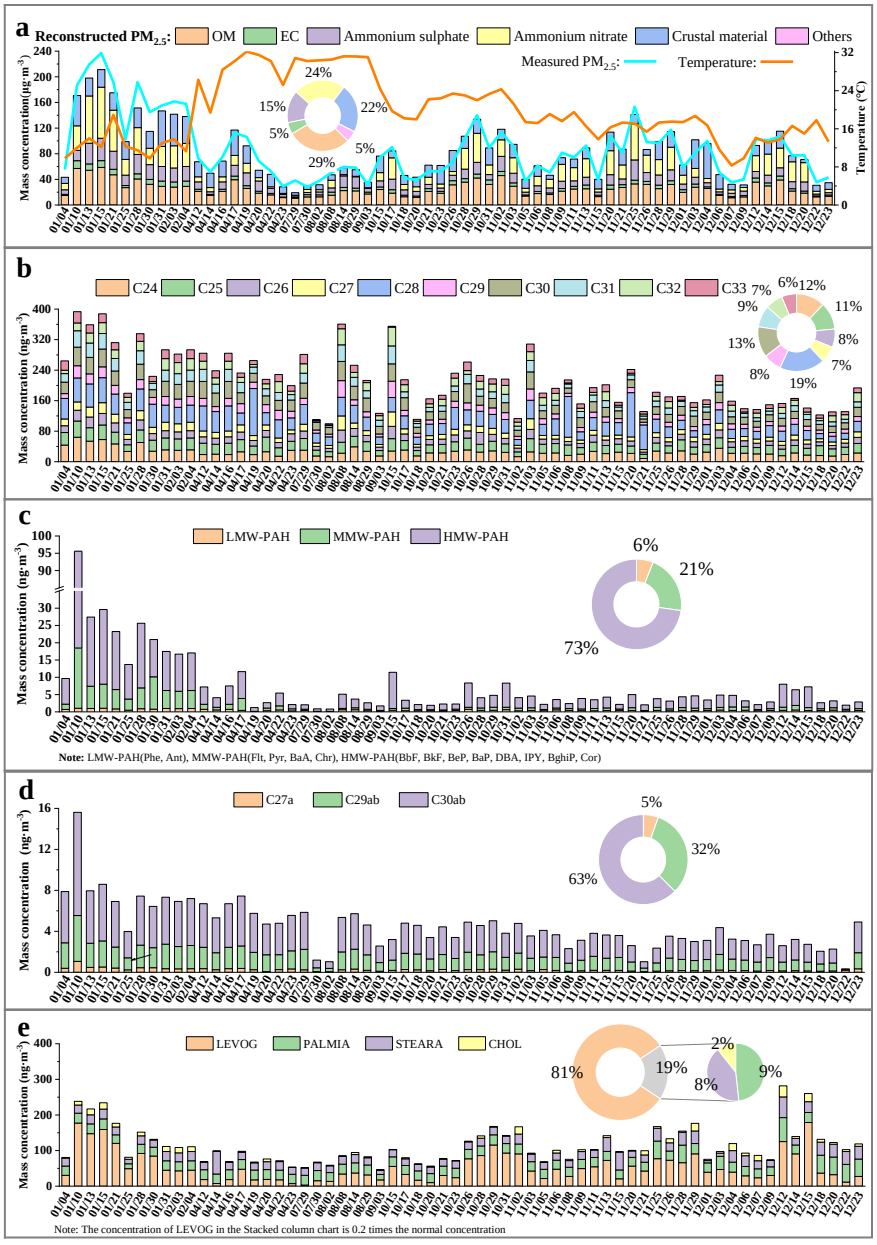

735

736 **Figure 1.** The daily concentrations of $PM_{2.5}$, mass closure of main species, and organic components.
737 (a) Mass closure of main species; (b) n-alkanes; (c) PAHs; (d) hopanes; (e) unsaturated fatty acids
738 and cholesterol.

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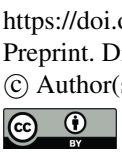

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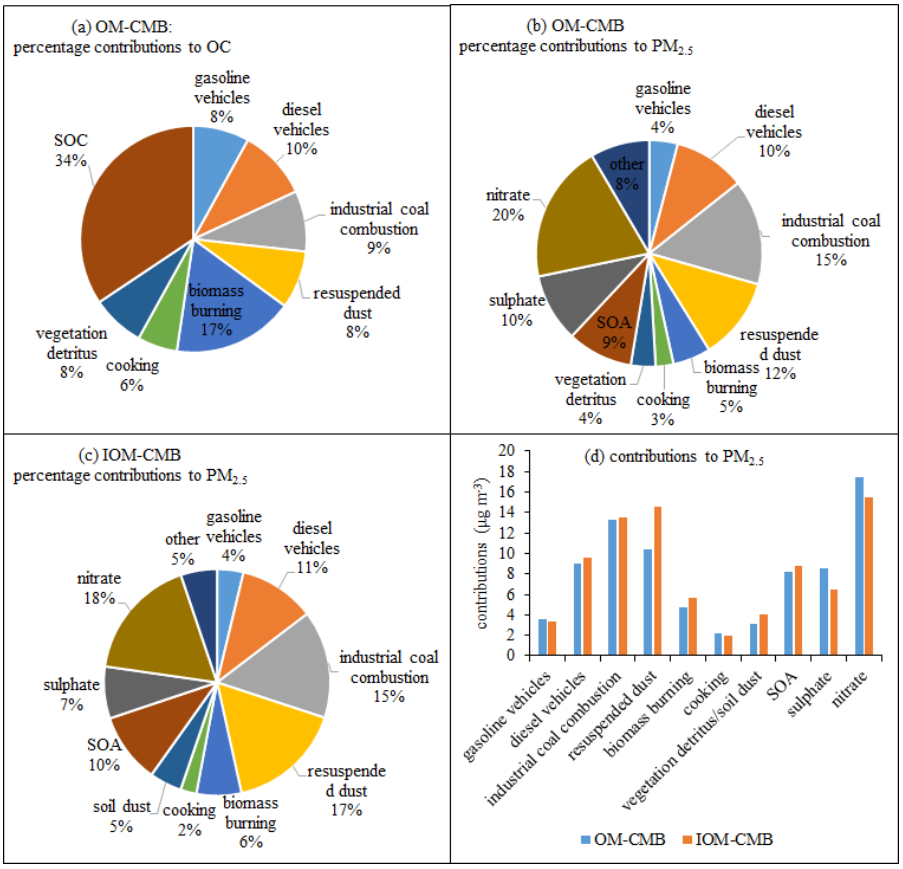

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740 **Figure 2.** (a) The average of percentage contributions to OC estimated by the OM-CMB; (b) The
741 annual average of percentage contributions to $PM_{2.5}$ estimated by the OM-CMB; (c) The annual
742 average of percentage contributions to $PM_{2.5}$ estimated by the IOM-CMB; (d) Comparison of
743 contributions to $PM_{2.5}$ estimated by the OM-CMB and IOM-CMB.
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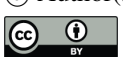

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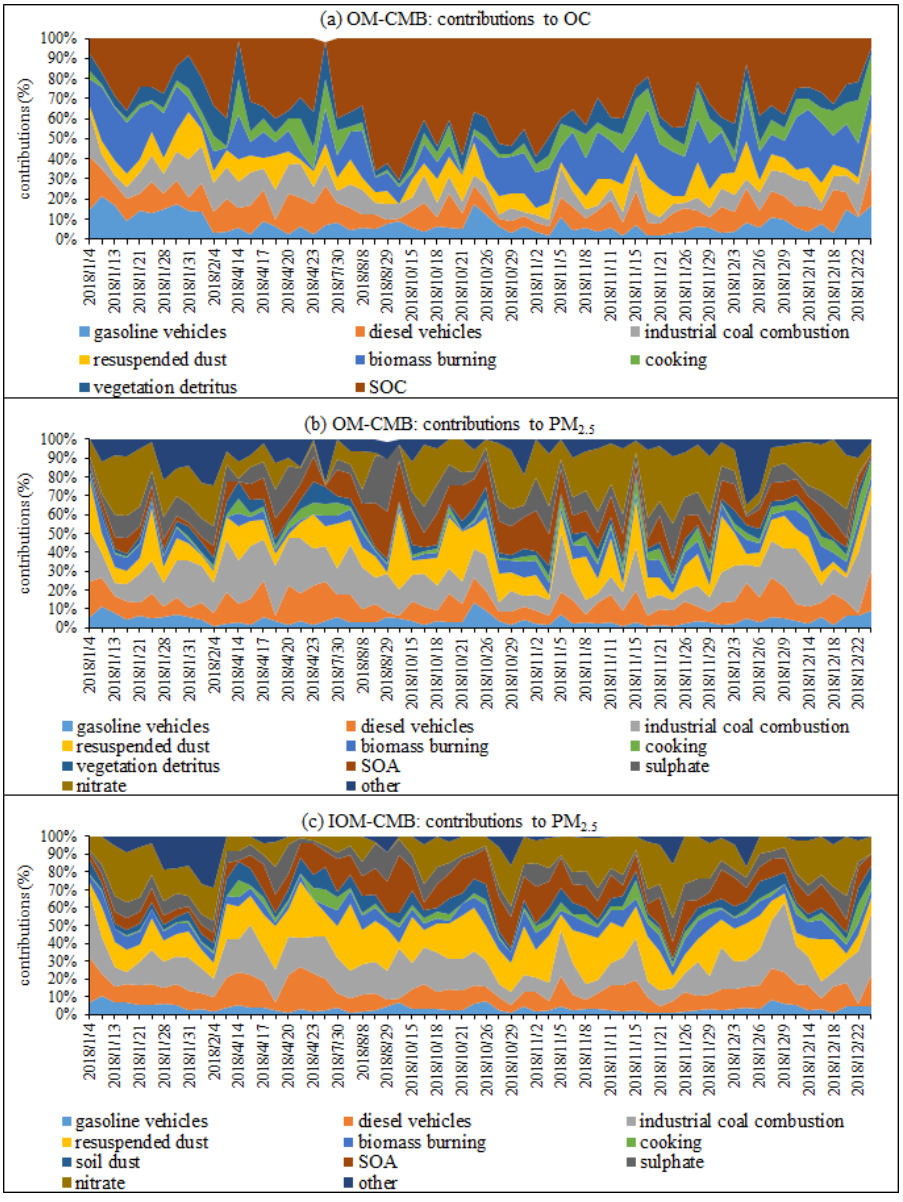

745

746 **Figure 3.** (a) Daily contributions to OC estimated by the OM-CMB; (b) Daily contributions to $PM_{2.5}$
747 estimated by the OM-CMB; (c) Daily contributions to $PM_{2.5}$ estimated by the IOM-CMB.
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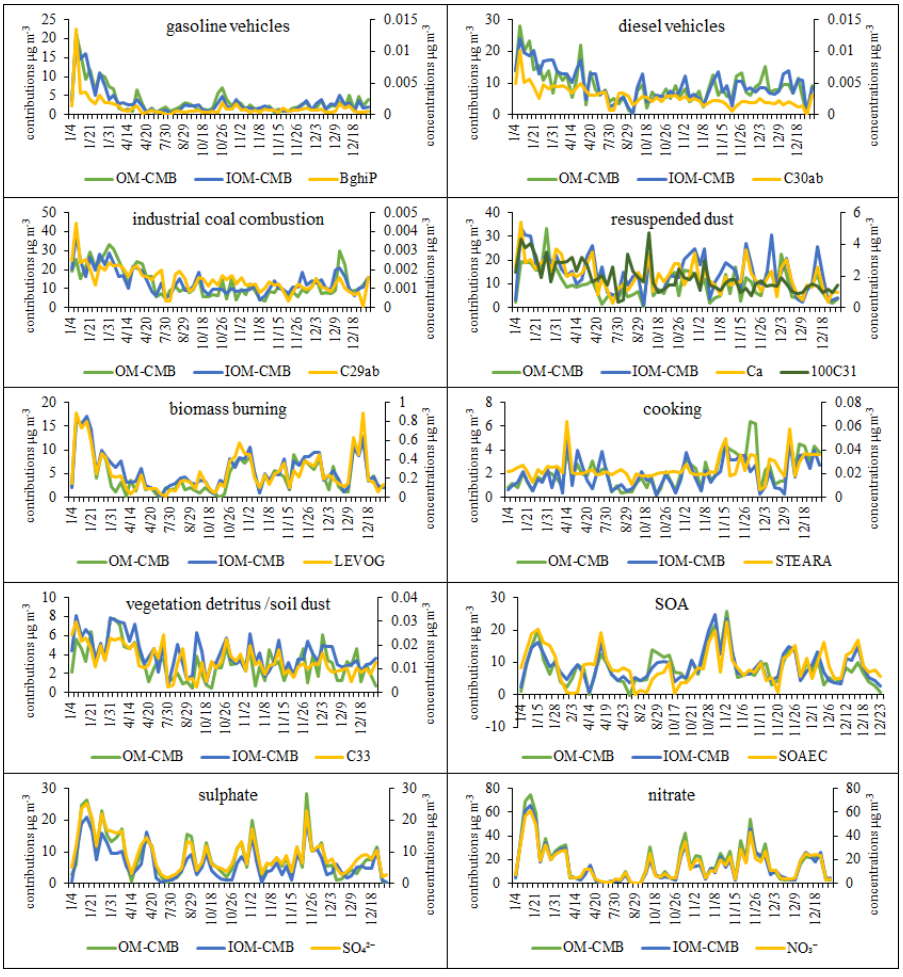

Figure 4. Comparisons among source contributions estimated by the OM-CMB and IOM-CMB, and corresponding markers.