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1 **Size-resolved source apportionment of particulate matter from a megacity in**
2 **northern China based on one-year measurement of inorganic and organic**
3 **components**

4

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16 **Abstract**

17 This research apportioned size-resolved particulate matter (PM) contributions in a
18 megacity in northern China based on a full year of measurements of both inorganic and
19 organic markers. Ions, elements, carbon fractions, n-alkanes, polycyclic aromatic
20 hydrocarbons (PAHs), hopanes and steranes in nine PM size fractions were analyzed.
21 High molecular weight PAHs concentrated in fine PM, while most other organic
22 compounds showed two peaks. Both two-way and three-way receptor models were used
23 for source apportionment of PM in different size ranges. The three-way receptor model
24 gave a clearer separation of factors than the two-way model, because it uses a
25 combination of chemical composition and size distributions, so that factors with similar
26 composition but distinct size distributions (like more mature and less mature coal
27 combustion) can be resolved. The three-way model resolved six primary and three
28 secondary factors. Gasoline vehicles and coal and biomass combustion, nitrate and high
29 relative humidity related secondary aerosol, and resuspended dust and diesel vehicles
30 (exhaust and non-exhaust) are the top two contributors to pseudo-ultrafine ($<0.43\mu\text{m}$),
31 fine ($0.43\text{-}2.1\ \mu\text{m}$) and coarse mode ($>2.1\ \mu\text{m}$) PM, respectively. Mass concentration
32 of PM from coal and biomass combustion, industrial emissions, and diesel vehicle
33 sources showed a bimodal size distribution, but gasoline vehicles and resuspended dust
34 exhibited a peak in the fine and coarse mode, separately. Mass concentration of sulphate,
35 nitrate and secondary organic aerosol exhibited a bimodal distribution and were
36 correlated with temperature, indicating strong photochemical processing and
37 repartitioning. High relative humidity related secondary aerosol was strongly associated

38 with size shifts of PM, NO₃⁻ and SO₄²⁻ from the usual 0.43-0.65 μm to 1.1-2.1 μm. Our
39 results demonstrated the dominance of primary combustion sources in the <0.43μm
40 particle mass, in contrast to that of secondary aerosol in fine particle mass, and dust in
41 coarse particle mass in the Northern China megacity.

42 **Keywords:** particulate matter, size-resolved source apportionment, three-way factor
43 analysis model, organic marker

44

45

46

47 **1. Introduction**

48 The mortality effects, morbidity effects, visibility and regional radiative forcing due
49 to atmospheric particulate matter (PM) vary with particle size and chemical
50 composition (Kelly and Fussell 2012; Pedersen et al., 2016). Size-resolved chemical
51 composition can provide useful information for size-resolved source apportionment
52 (Tian et al., 2016; Liu et al., 2017; Masiol et al., 2017; Beddows et al., 2019; Hilario et
53 al., 2020). Components in different size fractions can serve as markers for different
54 sources. For example, the PM_{1.0} fraction of K mostly originates from fuel burning, but
55 K is attributed to dust or sea spray in coarse PM (Viana et al., 2008). Thus,
56 understanding the size distribution and size-resolved chemical composition is crucial
57 for determining the sources, formation mechanisms and atmospheric processing of the
58 particles (Guo et al., 2014; Tian et al., 2016; Hilario et al., 2020).

59 Certain organic compounds in the PM can be used as tracers for particular sources

60 (Harrison, 1996). N-alkanes, polycyclic aromatic hydrocarbons (PAHs), hopanes and
61 steranes have been shown to assist in distinguishing PM sources (Oros and Simoneit,
62 2000; Ke et al., 2008; Pereira et al., 2017), and these compounds might also be used to
63 best advantage in combination with other data (elements, ions and carbon fractions) by
64 simultaneously determining the organic and inorganic composition (Harrison, 1996).
65 Several studies have shown that the size distribution of organic compounds in PM can
66 provide critical information for determining sources and atmospheric processes (Han et
67 al., 2018; Wang et al., 2009). However, studies on the size-resolved source
68 apportionment based on joint inorganic and organic components are very limited,
69 especially those including nine sizes, ranging from <0.43 to 10 μm , and an entire year
70 of measurement.

71 Receptor-based models have been widely applied to quantitatively apportion sources
72 of PM, e.g., positive matrix factorization, PMF (Paatero and Tapper, 1994). Such
73 apportionments are typically performed for a single size fraction. Some studies have
74 applied PMF to apportion the sources in PM of multiple sizes (Contini et al., 2014;
75 Karanasiou et al., 2009; Visser et al., 2015). The usual approach for apportioning size-
76 resolved component data is to separately undertake calculations for each size fraction,
77 or to simply combine the data into one or more size modes (Wang et al., 2016; Tian et
78 al., 2016; Hilario et al., 2020), losing the size-composition variation of source profiles
79 (Dodd et al., 1991; Ma et al., 2016; Jia et al., 2018; Wang et al., 2018) or failing to
80 investigate the detailed size distributions of source contributions. Thus, data that
81 contains both size and compositional information requires advanced analysis tools

82 (Pere-Trepat et al., 2007). A three-way factor analysis model (named the ABB model
83 here) to apportion sources across multiple size fractions has been explored in the
84 literature and our previous work (Pere-Trepat et al., 2007; Shi et al., 2015; Liu et al.,
85 2018), demonstrating that the three-way factor analysis model permits the extraction
86 of maximal information from size-resolved data (Shi et al., 2015; Tian et al., 2016; Liu
87 et al., 2018). Bernardoni et al. (2017) used the three-way model to apportion size-
88 segregated samples during wintertime in Italy and two traffic sources were identified
89 due to different size-segregated profiles. Therefore, both size fractionated data and
90 chemically speciated data with inorganic and organic markers can enhance the source
91 resolution.

92 In this study, we measured water-soluble ions, elements (Al, Ca, Ti, K, Mg, Na, V,
93 Fe, Cu, Zn, Mn, Pb, As, Cd, Co, Cr, and Ni), carbon fractions, n-alkanes, PAHs, hopanes
94 and steranes in size-resolved PM (9 stages) samples collected from May 2018 to April
95 2019 in a megacity (Tianjin) in northern China. The objectives were: (1) to explore how
96 to better apportion the sources of aerosols based on size-resolved inorganic and organic
97 components, and make a methodological comparison of the three-way ABB model and
98 EPA PMF model for size-resolved source apportionment; (2) to investigate the size
99 distributions of aerosol sources, and to understand the relationships among sources and
100 meteorological parameters. The source apportionment of PM_{2.5} or PM₁₀ (PM with
101 aerodynamic diameter of ≤ 2.5 or $10 \mu\text{m}$) has been reported in Tianjin (Tian et al., 2014
102 and 2018; Wen et al., 2018). However, no size distribution of sources was studied. This
103 study differs in apportioning a whole year measurement dataset which is both size

104 fractionated and chemically speciated with joint organic and inorganic markers. In
105 doing so, we demonstrated that the size-resolved receptor modelling of joint inorganic
106 and organic markers can give more robust apportionment of source categories and
107 enhance the understanding of physicochemical processing of PM. We also showed the
108 advantages in the simultaneous apportionment by composition and particle size
109 achieved with the ABB model.

110

111

112 **2. Method and materials**

113 *2.1. Study area and sampling*

114 The sampling site (Figure S1) was located in Tianjin which is in the North China
115 Plain. The details of Tianjin and sampling sites are provided in **section I of**
116 **Supplementary Material (SM)**. Studies on emission inventory and source
117 apportionment for the Tianjin or Beijing-Tianjin-Hebei (BTH) region **are summarized**
118 **in section I of the SM, and provide further information on receptor modeling.**

119 Nine-stage PM samples were collected by an Andersen air sampler (Andersen Series
120 E-0162, USA) with quartz-fibre filters (81 mm in diameter, Pall Life Sciences, USA).

121 The nine sizes were < 0.43, 0.43–0.65, 0.65–1.1, 1.1–2.1, 2.1–3.3, 3.3–4.7, 4.7–5.8,
122 5.8–9.0, and >9.0 μm . Three modes were defined as coarse (>2.1 μm), fine (0.43–2.1
123 μm), and pseudo-ultrafine (< 0.43 μm) modes.

124 A total of 73 sets of size-resolved samples (total 657 PM samples) were used in this
125 work, collected in spring (May 2018, March 2019 and April 2019), summer (June and

126 August 2018), autumn (1 September to 15 November 2018) and winter (15 November
127 2018 to 15 March 2019).

128

129 *2.2. Chemical analysis and data description*

130 The filters were weighed with an electronic microbalance (Mettler Toledo,
131 Switzerland) before and after sampling, after being equilibrated. Seven ions, 17
132 elements, 7 carbon fractions, 18 PAHs, 2 cholestanes, 7 hopanes and 24 n-alkanes were
133 analyzed. Ion concentrations, including Na^+ , K^+ , Ca^{2+} , NH_4^+ , Cl^- , NO_3^- and SO_4^{2-} , were
134 analyzed by a Thermo ICS900 Ion Chromatograph (Thermo Electron, USA). Elements
135 were analyzed by inductively coupled plasma-mass spectrometry (ICP-AES) (IRIS
136 Intrepid II, Thermo Electron, USA). Carbon fractions (OC1, OC2, OC3, OC4, OP, EC1,
137 EC2, EC3) were analyzed by a thermal/optical carbon aerosol analyzer (DRI 2001A,
138 Atmoslytic Inc., USA), using the IMPROVE-A thermal/optical reflectance (TOR)
139 protocol. Organic compounds were analyzed by gas chromatography-mass
140 spectrometry (GC-MS, Agilent Technology). A DB-5MS fused-silica capillary
141 column and EI mode were used in the GC-MS. More details of chemical analysis are
142 provided in **section II of the SM**. The full names, corresponding abbreviations and
143 detection limits of all determined components are summarized in Table S1.

144 To ensure quality assurance and control, the same instruments and methods were
145 used for all samples. Standard reference materials of corresponding components (and
146 potassium hydrogen phthalate for OC and EC) were analyzed with the same procedure
147 and showed good accuracy and low relative standard deviations. Each sample was

148 extracted twice, which was analysed with GC-MS to determine the concentration of
149 organic compounds. Internal standards were used for the samples to qualify actual
150 volumes of the target compounds present. The calibration curves were strongly linear
151 with correlations being 0.99 or 0.999. Detailed information on Quality assurance and
152 quality control are provided in **section III of the SM**. The correlation plots between
153 PM_{2.1} and PM₁₀ mass concentrations sampled by the Andersen sampler (PM-measured)
154 vs corresponding means of continuous PM_{2.5} and PM₁₀ concentrations monitored by
155 the BPM (PM-monitor) are shown in Figure S2. High correlations (0.86 and 0.82) were
156 observed.

157 Meteorological parameters, including wind speed (WS, m s⁻¹), wind direction (WD),
158 temperature (T, °C), relative humidity (RH, %), and pressure (P, Pa), were
159 simultaneously monitored by the local Micro Meteorological Station (WS600–UMB,
160 LUFFT, Germany).

161

162 2.3. ABB three-way receptor model

163 The three-way receptor model estimates one contribution pattern matrix (matrix A)
164 for all inputted PM sizes, and independent source profile matrices (matrix B), so it was
165 named the ABB model. Source compositions are particle size dependent. The principle
166 of this model is as follows:

$$167 \quad x_{ijk} = \sum_{p=1}^P a_{ip} b_{jpk} + e_{ijk} \quad (1)$$

168 where x_{ijk} is the concentration of the j th component in the i th sample at the k th size; a_{ip}
169 is associated with contribution pattern of the p th source to the i th sample; b_{jpk} is fraction

170 of the j th component in the p th source composition at the k th size; e_{ijk} is the residual of
171 the j th component in the i th sample at the k th size. The ABB model was performed on
172 a script for the general multilinear problem solver, the Multilinear Engine 2 (ME2)
173 (Pere-Trepat et al., 2007; Liu et al., 2018).

174 ME2 provides several options (error model, EM) to calculate u_{ijk} (Paatero, 2007). In
175 this work, EM=-14 was chosen, as is recommended for environmental data (Lee et al.,
176 1999; Paatero, 2007) and according to this error model, the u_{ijk} values are heuristically
177 computed from:

$$178 \quad u_{ijk} = C_1 + C_3 \max(|x_{ijk}|, |\sum_{p=1}^P a_{ip} b_{jpk}|) \quad (3)$$

179 where C_1 and C_3 are user-specified parameters, which were 0.2 and 0.00002 in this
180 work (Lee et al., 1999). The final contributions were calculated through the regression
181 of PM mass concentration matrix and source contribution matrix.

182 When selecting variables, the variables with 1/3 data below DL were not used. If
183 some components showed similar size distributions and temporal variations, and
184 indicated consistent sources, sums of them were used. Thus, the following species were
185 inputted for receptor modeling: Cl^- , NO_3^- , SO_4^{2-} , NH_4^+ , Al, Ca, Ti, Fe, Cu, Na, K, Mn,
186 Pb, OC1, OC2-4 (sum of OC2, OC3 and OC4), EC1, EC2-3 (sum of EC2 and EC3),
187 three-ring PAHs (sum of Any, Ana, Flu, Phe, and Ant), four-ring PAHs (sum of Flt,
188 Pyr, BaA and Chr), BbF, BkF, BaP, DBA, IPY, BghiP, Cor, C29 $\alpha\beta$ hopane, C30 $\alpha\beta$
189 hopane, C30 $\beta\beta$ +C34 $\alpha\beta$ R hopane, C15-18+C28 (sum of C15, C16, C17, C18 and C28
190 n-alkanes), C19-20 (sum of C19 and C20 n-alkanes), C23-26 (sum of C23, C24, C25
191 and C26 n-alkanes), and C31 n-alkane. Their full names are shown in Table S1. The

192 missing data were replaced by the mean of the adjacent data, and the BDL were replaced
193 by the half of DL.

194 In this work, nine (number of sizes) parallel matrices of 73 (number of samples) ×
195 33 (number of variables as listed in section 2.1) were inputted into the ABB model. The
196 three-way model calculates all the nine sizes at the same time, and the outputs were
197 nine independent factor profile matrices as well as contributions of each size with same
198 variation but different values. The fitting plot between the measured and estimated PM
199 mass concentrations (the sum of contributions apportioned to each identified source
200 category) is shown in Figure S3. It shows that the ABB model was able to effectively
201 evaluate the PM concentrations at all sizes, with the slope being 1 and Pearson's r being
202 0.80. The scaled residuals were in the range of -3 to 3 (Figure S4).

203 The information on the EPA PMF 5.0 receptor model is provided in **section IV in the**
204 **SM.**

205

206 **3. Results and discussion**

207 *3.1. Size-resolved chemical compositions*

208 Concentrations of chemical species in the pseudo-ultrafine, fine and coarse modes
209 during the four seasons are shown in Figure 1a and the reconstructions of chemical
210 species are shown in Figure S5. The largest components were organic carbon fraction
211 OC3, NO₃⁻, and crustal elements (sum of Al, Ca, Fe and Ti) in the pseudo-ultrafine, fine
212 and coarse modes, respectively. The size distributions (dC/dlogDp) of the main
213 components are shown in Figure S6a. NO₃⁻, SO₄²⁻ and NH₄⁺ mass concentrations were

214 abundant in the fine mode, which exhibited maxima at 0.43-1.1 μm . Tian et al. (2016)
215 also found that ions exhibited maxima at 0.43–0.65 or 0.65–1.1 μm . The size
216 distributions of Cl^- showed a strong peak in the fine mode associated with emissions of
217 HCl from combustion sources which can form semi-volatile ammonium chloride (Pio
218 and Harrison, 1987), and a weak peak in the coarse mode because of sea salt. Carbon
219 fractions generally exhibited typical bimodal distributions with peaks in both fine and
220 coarse modes. The crustal elements (Al, Ca, Fe, and Ti) were primarily concentrated in
221 the coarse mode at 4.7-9.0 μm , which is consistent with previous studies (Tian et al.,
222 2016; Hilario et al., 2020).

223

224 3.2. Size-segregated organic compounds

225 Figure 1b to Figure 1d describe the concentrations of organic compounds in PM, and
226 the size distributions ($dC/d\log D_p$) of the organic component concentrations are shown
227 in Figure S6b and S6c. The 3-ring PAHs showed a bimodal size distribution, while most
228 other PAHs were strongly concentrated in the fine mode. Previous studies also reported
229 a bimodal distribution of low molecular weight PAHs and a strong peak in the fine
230 mode of high molecular weight PAHs (Lv et al., 2016; Han et al., 2018). High molecular
231 weight PAHs are less volatile and predominantly formed on smaller particles where
232 they condense immediately after combustion. However, low molecular weight PAHs
233 are more volatile, so they are easily adsorbed on larger particles as the emissions cool
234 down, or can evaporate from the particle-phase into the air and subsequently
235 adsorb/condense onto pre-existing coarser particles (Offenberg and Baker, 1999). Most

236 steranes, hopanes and n-alkanes showed two peaks at 0.43-1.1 μ m in the fine mode and
237 3.3-5.8 μ m in the coarse mode. The bimodal distribution of most n-alkanes was
238 observed by Wang et al. (2009), Lyu et al. (2017) and Xu et al. (2017). The size
239 distributions of hopanes were reported as unimodal in the fine mode (Kleeman et al.,
240 2008; Han et al., 2018), and can be bimodal during summer (Wang et al., 2009).

241

242 3.3. Size-resolved source apportionment by the ABB three-way model

243 For the ABB three-way modeling, different factor numbers were tried to choose the
244 optimal number of factors. Considering studies on emission inventory and PM_{2.5} source
245 apportionment (Tian et al., 2016; Qi et al., 2017; Li et al., 2018; Xu et al., 2019) in the
246 **section I of the SM**, we found that nine factors gave best results, because too few factors
247 would cause a mixed factor with different source categories (for example, a mixed
248 factor of gasoline, coal and biomass combustion was estimated in the eight-factor
249 solution), whereas too many factors would result in factors that are difficult to interpret.
250 Figure 2 shows the factor profiles (composition as % of species sum) of PM at nine size
251 ranges. Figure 3 describes the mass and percentage source contributions in three modes,
252 and Figure 4 the size distributions (dC/dlogDp) of factor contributions at nine size
253 ranges.

254 3.3.1. Factor 1: coal and biomass combustion (CBC)

255 The profiles of the factor 1 were similar for sizes <0.43, 0.43–0.65, 0.65–1.1 and
256 1.1–2.1 μ m, accounting for a high proportion of Cl⁻ (44–68% of total Cl⁻), OC1
257 (33–42%), EC1 (27–41%), four-ring PAHs (48–68%) and C15–18+C28 n-alkanes, as

258 well as moderate OC₂₋₄, crustal elements, K, Cor, C_{29αβ} and C_{30αβ}. The factor
259 profiles (Figure 2a) were similar at sizes 2.1–3.3, 3.3–4.7, 4.7–5.8 and 5.8–9.0 μm with
260 moderate loadings of Cl⁻, carbon fractions, crustal elements and four-ring PAHs. This
261 factor profile is similar to the source profiles of coal combustion, characterized by
262 carbon fractions, crustal elements and Cl⁻ (Bi et al., 2019). Cl⁻ was found in this factor
263 since emissions of HCl from coal and biomass combustion can form semi-volatile
264 ammonium chloride (Pio and Harrison, 1987). The four-ring PAHs, C₁₅₋₁₈ n-alkanes
265 and hopane have also been reported as organic markers of coal combustion (Bi et al.,
266 2008; Zhang et al., 2008). As discussed above, four-ring PAHs and C₂₈ n-alkane are
267 significantly enhanced during winter, suggesting that they are indicative of coal
268 combustion due to heating in Tianjin and surrounding regions. Higher molecular weight
269 n-alkanes (like C₂₈ here) may be predominantly of a vascular plant wax origin
270 entrapped in the coals (Oros and Simoneit, 2006). K or K⁺, Cl⁻, OC and three- and
271 four-ring PAHs may also arise from biomass combustion (Hays et al., 2005; Shen et
272 al., 2011), so this factor likely contains a contribution from biomass combustion. Large
273 scale biomass combustion is prohibited in Tianjin, so biomass combustion may be not
274 an important source. Thus, factor 1 is identified as coal and biomass combustion (CBC).

275 As shown in Figure 3, the CBC contributed 21%, 14% and 12% in the pseudo-
276 ultrafine, fine and coarse modes, respectively. Previous studies (Tian et al., 2016; Wang
277 et al., 2016) consistently reported that coal combustion contributed higher fractions in
278 fine PM than in coarse PM in Beijing and Tianjin. According to Figure 4a, the size
279 distribution of the CBC mass contributions ($dC/d\log D_p$, μg m⁻³) was bimodal, with

280 peaks at 0.43–1.1 μm and 5.8–9.0 μm .

281 Figure S7a shows a clear seasonal variation of the CBC. A larger contribution (66
282 $\mu\text{g m}^{-3}$ and 24% of PM_{10} as shown in Figure S8) was observed in the winter, which is
283 associated with intensive coal combustion for residential heating and industrial
284 activities (Vu et al., 2019). Coal is one of the most important energy sources for
285 industries and residential activities in Northern China according to the China Energy
286 Statistical Yearbook (CESY, 2019). According to the correlations between source
287 contributions and meteorological parameters in Table S2, the mass contributions of the
288 coal and biomass combustion source showed a negative correlation with temperature
289 (Pearson's $r=-0.52$ at 0.01 level), consistent with the key role of heating in the emission
290 of this source.

291

292 3.3.2. Factor 2: coal combustion (CC)

293 Factor 2 is characterized by high $\text{C30}\beta\beta+\text{C34}\alpha\beta\text{R}$, four-ring PAHs and carbon
294 fractions at sizes 1.1–5.8 μm (Figure 2b). $\text{C30}\beta\beta$ and $\text{C34}\alpha\beta\text{R}$ are regarded as markers
295 of less mature coals, such as lignite and sub-bituminous coal combustion (Oros and
296 Simoneit, 2000), so factor 2 is identified as the other coal combustion (CC). Its
297 percentage contributions accounted for 2% in the pseudo-ultrafine and 4% in the fine
298 and coarse modes (Figure 3), and its size distributions showed a strong peak at 3.3–5.8
299 μm (Figure 4b). This factor made relatively higher contributions during early
300 November and early March, which were the beginning and end of the heating season.

301 In general, the combustion of coal in China can be divided in two types: efficient

302 centralized coal combustion and scattered coal burning (Shi et al., 2020). The former
303 refers to coal used for power generation, heat supply, and large-scale industrial boilers,
304 while the latter refers to coal utilization for domestic purposes such as heating and
305 cooking. Scattered coal combustion with lower combustion efficiency and pollution
306 control deficiency has been found to be an important source in the winter in northern
307 China (Shi et al., 2020). In Tianjin, coal fired central heat supply is generally
308 implemented, while at the beginning and end of the heating season, heating boilers may
309 run at low combustion efficiency, so scattered coal may be used for household stoves.
310 The low combustion temperature and poor combustion efficiency of coals in household
311 stoves may lead to incomplete combustion and generate relatively large particles (Wang
312 et al., 2018; Wu et al., 2018). Bimodal distributions of organic components in coal
313 combustion from a circulating fluidized bed boiler have been reported, peaking at
314 2.1–1.1 μm and 5.8–4.7 μm (Wang et al., 2018), indicating that coal combustion with
315 a low combustion temperature can generate relatively large particles. **Factor 1** was from
316 general coal and biomass combustion including all coal types, while **Factor 2** was
317 associated with less mature coals. The latter was extracted in this study because of its
318 unique pattern of size distribution. Similarly, **Bernordi et al. (2017) identified two**
319 **sources of traffic particles according to their size distribution using the three-way**
320 **receptor model.**

321

322 3.3.3. Factor 3: gasoline vehicles (GV)

323 Factor 3 is characterized by the high weights of OC2–4, DBA, IPY, BghiP and

324 C23–26 n–alkanes, which were similar at sizes <0.43, 0.43–0.65, 0.65–1.1, 1.1–2.1,
325 2.1–3.3, 3.3–4.7 and 4.7–5.8 μm , and only by some Pb at sizes 5.8–9.0 and >9.0 μm
326 (Figure 2c). It has been reported that gasoline vehicles emit heavier PAHs (Phuleria et
327 al., 2006) and C25–C26 n–alkanes (Schauer et al., 1999 and 2002).

328 The percentage contributions (Figure 3) of the gasoline vehicle generally decreased
329 with the increasing sizes, contributing 22%, 10% and 4% in pseudo-ultrafine, fine and
330 coarse modes, respectively. It showed a unimodal size distribution peaking in the fine
331 mode (0.43–1.1 μm) (Figure 4c). The percentage contributions of the gasoline vehicle
332 exhibited weak seasonal variation (Figure S8).

333

334 3.3.4. Factor 4: diesel vehicles (DV)

335 Factor 4 is characterized by high loading of EC2+EC3, BbF, BkF and C19–20
336 n–alkanes at most sizes and also weakly linked with SO_4^{2-} , NH_4^+ , Cu, Fe and Mn at
337 sizes > 2.1 μm (Figure 2d), and was identified as diesel vehicles. Kim and Hopke (2004)
338 demonstrated that diesel emissions contain a high concentration of EC2. Diesel vehicles
339 generally emit relatively more light PAHs (Phuleria et al., 2006), and the n–alkanes in
340 highest abundance were found to be C20 for diesel vehicles (Schauer et al., 1999 and
341 2002). In addition, Cu, Fe and Mn in factor 4 may be caused by brake and tire wear,
342 and SO_4^{2-} may be partly associated with sulphur in diesel fuel (Wei et al., 2019), which
343 can be resuspended through road dust. Thus, Factor 4 is associated with diesel engine
344 emissions and related non-exhaust particles. In China, diesel vehicles are usually heavy
345 trucks which can also cause strong non-exhaust particles, such as road dust, brake and

346 tire wear, so they have similar temporal variations and were extracted as a single mixed
347 factor by the ABB model.

348 The percentage contributions of the diesel vehicle factor were 15%, 9% and 20% in
349 the three modes (Figure 3), and its mass contributions showed a bimodal size
350 distribution, peaking at 0.43–0.65 μm and 5.8–9.0 μm (Figure 4d). Referring to the
351 factor profiles, the contributions were mainly associated with diesel vehicles in the fine
352 mode and associated with non-exhaust in the coarse mode. The percentage
353 contributions of the diesel vehicle also exhibited weak seasonal variation (Figure S8),
354 which were in the range of 17% (spring) – 13% (summer) for PM_{10} .

355

356 3.3.5. Factor 5: resuspended dust (RD)

357 Factor 5 is characterized by large percentage contributions to Al, Ca, Ti, Na, and C31
358 at most sizes (Figure 2e). Al, Ca and Ti are typical crustal elements and thus this factor
359 is attributed to resuspended dust. High contributions to Na at most sizes and minor
360 contributions of Cl^- in the coarse mode can indicate sea salt. The C31 mainly originates
361 from plant wax and a tire–wear source (Han et al., 2018). Thus, this factor may be
362 ascribed to both natural origins (such as windblown crustal dust, sea salt, and vegetation
363 sources) and anthropogenic causes (such as construction of buildings and roads).

364 The percentage contributions of resuspended dust were low in the pseudo-ultrafine
365 mode (7%) and high in the coarse mode (26%) (Figure 3). Some studies have reported
366 that resuspended dust contributed markedly higher fractions in coarse PM than in fine
367 PM (Tian et al., 2016; Wang et al., 2016). The size distribution of mass contributions

368 (dC/dlogDp) of this factor was unimodal at 3.3–5.8 μm (Figure 4e). The resuspended
369 dust contributions showed a clear temporal variation with high contributions in spring
370 and summer (Figure S8). It contributed 29%, 36%, 18% and 12% of PM₁₀ during spring,
371 summer, autumn and winter, respectively. As shown in Figures S9, resuspended dust
372 contributions were high when wind speeds were strong. Stronger winds improve the
373 dispersion of PM, but also can result in the resuspension of dust. Dry surfaces and
374 strong wind speeds and vegetation impacts during spring and summer can explain the
375 higher contributions of this factor.

376

377 3.3.6. Factor 6: industrial emissions (IE)

378 Factor 6 is characterized by high fractions of metals, including Ca, Fe, Cu, Mn, Pb
379 at most size ranges (Figure 2f). Carbon fraction OC1 and some organic components
380 also showed strong influences in this factor. This is attributed to industrial emissions.
381 Fe, Cu, Mn and Pb are tracers for PM emissions from the steel industry, and Ca for the
382 building materials industry. Carbonaceous materials are associated with the combustion
383 processes within the industrial emissions. Tianjin, as an industrial megacity in Northern
384 China, has many industries, such as the steel industry, building materials industry, and
385 petrochemical industry. The productions of crude steel, pig iron and cements were about
386 20, 16 and 6.9 million tons in 2018 (Database of China Business Industry Research
387 Institute, 2018).

388 Its percentage contributions were 13%, 11% and 17% from pseudo-ultrafine to coarse
389 modes (Figure 3), and its mass concentration showed a bimodal size distribution with

390 peaks at 0.43–0.65 and 3.3–5.8 μm (Figure 4f). The contributions showed weak
391 temporal variations (Figure S7f). Seasonal average contributions to PM_{10} ranged from
392 14 $\mu\text{g m}^{-3}$ (summer) to 39 $\mu\text{g m}^{-3}$ (winter), and its percentage contributions were 10%
393 of PM_{10} during summer and about 14% during other seasons.

394

395 3.3.7. Factor 7: nitrate (NI)

396 Factors 7, 8 and 9 were all associated with secondary formation. It is not unusual to
397 divide secondary particles into different factors based on their size distribution and
398 temporal variations, reflecting different formation pathways (Kim et al., 2007;
399 Bernardoni et al., 2017; Wang et al., 2018; Dai et al., 2020).

400 Factor 7 is characterized by high NO_3^- and NH_4^+ at sizes $< 2.1 \mu\text{m}$, as shown in
401 Figure 2g. This factor is attributed to “nitrate” aerosol. Its contribution was high at sizes
402 0.43–2.1 μm and showed a strong peak at size 0.65–1.1 μm (Figure 4g), contributing
403 9%, 16% and 5% in the pseudo-ultrafine, fine and coarse modes (Figure 3). The mass
404 concentrations of this factor were low during summer (Figure S8), due to the
405 thermodynamic instability of ammonium nitrate.

406

407 3.3.8. Factor 8: sulphate, nitrate and SOA (SNO)

408 Factor 8 is characterized by high contributions of SO_4^{2-} and NH_4^+ at sizes $< 1.1 \mu\text{m}$,
409 NO_3^- at sizes $> 4.3 \mu\text{m}$, and moderate OC concentrations at sizes 0.43–2.1 and > 5.8
410 μm (Figure 2h). This factor is attributed to sulphate, nitrate and SOA (secondary organic
411 aerosol). The percentage contributions (Figure 3) of the SNO factor were higher (7-8%)

412 in the pseudo-ultrafine and fine modes than in the coarse mode (5%). The mass
413 concentration of this factor showed a bimodal size distribution peaking at 0.43–1.1
414 (mainly sulphate) and 5.8–9.0 μm (mainly nitrate) as shown in Figure 4h.

415 Contributions of this factor were notably high during summer (Figure S8), and
416 significantly correlated with temperatures (Pearson's $r=0.74^{**}$ as shown in Table S2
417 and Figure S9). When temperatures were high, photochemical processes are more
418 efficient, favouring gas phase oxidation of sulphur dioxide, leading to high sulphate in
419 the fine mode (John et al., 1990). The OC fractions in this factor may be associated with
420 secondary organic carbon (SOC). Due to the complexity of SOC formation and
421 partitioning, high temperatures may enhance the formation of some SOC in the fine
422 mode, and reapportion some SOC from the fine mode to the coarse mode. The NO_3^- in
423 Factor 8 was mainly observed in coarse mode, which was different with the fine nitrate
424 in Factor 7. This can be explained by their different formation pathways. Coarse NO_3^-
425 in Factor 8 can be explained by the pathway that high **temperature** can promote fine
426 mode NH_4NO_3 dissociation into vapour and then a shift onto coarse particles by
427 condensation, reaction, dissolution or coagulation (Hasheminassab et al., 2014), due to
428 the thermodynamic instability of NH_4NO_3 . The nitrate in Factor 8 showed similar
429 temporal variation with sulphate and SOA, so it was extracted together in this factor
430 (Wang et al., 2018).

431

432 3.3.9. Factor 9: high RH-related secondary aerosol (RHSA)

433 Factor 9 is characterized by high loadings of NO_3^- , SO_4^{2-} and NH_4^+ at sizes 1.1–3.3

434 μm (Figure 2i), and the size distribution of its contributions exhibited a strong peak at
435 1.1–2.1 μm (Figure 4i). According to the temporal variations of RH and contributions
436 of this factor in Figure S9, when the highest contributions occurred, the RH reached
437 about 90%. Thus, this factor was identified as a high RH-related secondary aerosol
438 (RHSA).

439 The RHSA contributions were high during periods of heavy pollution occurring
440 mainly in autumn and winter (Figure S7i). Figure 5(a) shows the size distributions of
441 measured PM, NO_3^- and SO_4^{2-} during high RHSA periods (RHSA contributions > 15
442 $\mu\text{g m}^{-3}$) and low RHSA periods in autumn and winter. RHSA mass contributions showed
443 a significant correlation with the ratios of concentrations of PM, NO_3^- and SO_4^{2-} at size
444 1.1–2.1 μm to those at 0.43–0.65 μm (Figure 5(b)), so this factor was strongly
445 associated with size shifts of PM, NO_3^- and SO_4^{2-} shifted from the usual 0.43–0.65 μm
446 to 1.1–2.1 μm during high RHSA periods.

447 The high RHSA contributions occurred at high RH and low WS (as shown in Figure
448 S9), which inhibits the dispersion of particles and their precursors, and favours the
449 formation of secondary particles and growth of hygroscopic particles. As PM
450 concentrations and RH increase simultaneously, the OH reactions slow down and the
451 aqueous-phase reactions start to play a more important role during some Chinese
452 winter haze episodes (Cheng et al., 2016). The size shifts of NO_3^- and SO_4^{2-}
453 demonstrate the more important role of aqueous-phase and heterogeneous reactions,
454 which are more likely to occur at relatively larger sizes (Zhang et al., 2013; Tian et al.,
455 2016). Relatively high elemental carbon (EC) was also observed in this factor at size

456 1.1–3.3 μm , likely due to the accumulation, coagulation and aging of primary particles.
457 It has been found that black carbon (BC)–containing particles tend to associate more
458 with secondary species during more polluted periods (Wang et al., 2019). The results
459 imply a strong link between EC and chemical aging, because EC provides active sites
460 for adsorption and reaction (Peng et al., 2016). In high RH atmospheric conditions,
461 hygroscopic growth can transform particles into microdroplets and enhances the rate of
462 formation of secondary particles (Cheng et al., 2008; Qu et al., 2015; Wang et al., 2020).

463

464 *3.4. Size–resolved source apportionment by EPA PMF 5.0: comparison with ABB* 465 *results*

466 Different solutions were tried for the EPA PMF 5.0 modeling. If PMF modelling was
467 done for each size fraction data, the results were unstable and not comparable. Thus,
468 the data for some sizes were combined according to the similarity of source
469 compositions. As shown in Figure S10, the factor profiles from the ABB model were
470 similar among sizes < 2.1 , $2.1\text{--}5.8$ and $5.8\text{--}10$ μm , so the EPA PMF 5.0 was performed
471 for three size combinations, based on 292 (number of samples at size <0.43 , $0.43\text{--}0.65$,
472 $0.65\text{--}1.1$ and $1.1\text{--}2.1$ μm) \times 33 (number of variables), 219 (number of samples at size
473 $2.1\text{--}3.3$, $3.3\text{--}4.7$, and $4.7\text{--}5.8$ μm) \times 33, and 146 (number of samples at size $5.8\text{--}9.0$
474 and >9.0 μm) \times 33 matrixes, respectively. The model was run 20 times for each size
475 combination. Three source composition matrices were obtained, as shown in Figure
476 S11. Different factor numbers were tried, and final factor numbers were determined
477 after considering source split and diagnostics. The error estimation diagnostics,

478 including Q, bootstrap (BS), displacement of factor elements (DISP), are listed in Table
479 S3. The regression plot (Figure S3) between measured and estimated PM
480 concentrations for EPA PMF 5.0 showed that the slope was 0.95 and Pearson's r was
481 0.83. As shown in Figure S11, six source categories (coal and biomass combustion,
482 gasoline vehicles, diesel vehicles, resuspended dust, industrial emissions, and
483 secondary aerosol) were identified for PM_{2.1} and PM_{2.1-5.8}, and five categories (coal and
484 biomass combustion, gasoline and diesel vehicles, resuspended dust, industrial
485 emissions, and secondary aerosol) were identified for PM_{5.8-10}.

486 The outcome of the EPA PMF5.0 analysis was compared with the ABB model results.
487 One of the significant differences was the factor numbers for the two models. The coal
488 combustion 2 and RHSA were resolved by the ABB model, but not by the EPA PMF5.0
489 model. The ABB model takes advantage of chemical composition, temporal variation
490 and size distribution to mine the intrinsic information of size-resolved joint inorganic
491 and organic components, so factors with unique variations of size distributions (such as
492 less mature coal combustion and RHSA in this work) are extracted.

493 For composition, the factor profiles of the nine sizes estimated by the ABB model
494 were combined into three sizes, and are shown in Figure S12. The factor profiles of
495 diesel vehicles from the two models are somewhat different, but those for the other
496 sources were similar. The correlations between temporal variations of contributions
497 estimated by the ABB model and the EPA PMF5.0 model are shown in Table S4,
498 suggesting that temporal variations of coal combustion (sum of coal and biomass
499 combustion and less mature coal combustion for the ABB model), resuspended dust,

500 and secondary aerosol (sum of nitrate, SNO, and RHSA for the ABB model) were
501 consistent. The temporal variations of gasoline vehicles and industrial emissions were
502 generally consistent at sizes where their contributions were high. The contributions of
503 diesel vehicles showed relatively large differences from the two methods.

504 Daily contributions for all sizes were obtained by the EPA PMF, and then, the average
505 of contributions for each size were calculated to show the size distributions of source
506 contributions in Figure 4. A relatively large difference was found for diesel vehicles in
507 the coarse mode, because non-exhaust particles of diesel vehicles were included more
508 in the resuspended dust factor for the EPA PMF5.0 model. The difference may result
509 from different principles and assumptions of the two models. The EPA PMF5.0 assumes
510 that the factor profiles were the same for each size in one run, so the road dust may be
511 mixed with resuspended dust due to more similar profiles. The ABB model assumes the
512 temporal variations of each source were the same for all sizes, so the diesel engine
513 emissions and related non-exhaust particles were extracted as a mixture because of their
514 similar temporal variation.

515 Different receptor models often give different results due to the inherent uncertainties
516 or limitations of the different models in PM source apportionment (Xu et al., 2021).
517 However, in this study, the size separation enabled us to obtain more consistent source
518 apportionment results from different models. This illustrates the value of doing source
519 apportionment on size-resolved PM.

520

521 **4. Conclusions**

522 Size-resolved source apportionment was conducted by two receptor models. We
523 found that primary combustion sources dominated in $<0.43\mu\text{m}$ particle mass, in
524 contrary to that of secondary aerosol in fine particle mass and dust in coarse particle
525 mass. For the size distributions, the CBC, IE and DV were bimodal; the GV was
526 unimodal in the fine mode; and the RD was unimodal in the coarse mode. The NI was
527 concentrated in the fine mode and was low during summer. The SNO significantly
528 correlated with temperature, indicating strong photochemical processing and
529 repartitioning. The RHSA factor characterized by high NO_3^- , SO_4^{2-} and NH_4^+ at sizes
530 $1.1\text{--}3.3\ \mu\text{m}$ significantly correlated with RH and peak shift. Comparison of the two
531 receptor models showed that the source profiles and size distributions of most sources
532 were generally consistent, especially at sizes with high contributions, which illustrates
533 the value of doing source apportionment on size-resolved PM. The three-way receptor
534 model gave clearer separation of factors than two-way model which separately analyzed
535 grouped size fractions, demonstrating the it can better mine size-resolved inorganic and
536 organic components, so factors with unique variations of size distributions (like CC and
537 RHSA) are extracted.

538

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