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Abstract

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

with size shifts of PM, NO_3^- and SO_4^{2-} from the usual 0.43-0.65 μm to 1.1-2.1 μm. Our results demonstrated the dominance of primary combustion sources in the <0.43μm particle mass, in contrast to that of secondary aerosol in fine particle mass, and dust in coarse particle mass in the Northern China megacity.

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

1. Introduction

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

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

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

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

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

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

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

2. Method and materials

2.1. Study area and sampling

The sampling site (Figure S1) was located in Tianjin which is in the North China Plain. The details of Tianjin and sampling sites are provided in section I of Supplementary Material (SM). Studies on emission inventory and source apportionment for the Tianjin or Beijing-Tianjin-Hebei (BTH) region are summarized in section I of the SM, and provide further information on receptor modeling. Nine−stage PM samples were collected by an Andersen air sampler (Andersen Series E−0162, USA) with quartz−fibre filters (81 mm in diameter, Pall Life Sciences, USA). 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, 5.8−9.0, and >9.0 μm. Three modes were defined as coarse (>2.1 μm), fine (0.43-2.1 μm), and pseudo-ultrafine (< 0.43 μm) modes.

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

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

2.2. Chemical analysis and data description

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

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

extracted twice, which was analysed with GC-MS to determine the concentration of organic compounds. Internal standards were used for the samples to qualify actual volumes of the target compounds present. The calibration curves were strongly linear with correlations being 0.99 or 0.999. Detailed information on Quality assurance and quality control are provided in section III of the SM. The correlation plots between $PM_{2.1}$ and PM_{10} mass concentrations sampled by the Andersen sampler (PM-measured) vs corresponding means of continuous $PM_{2.5}$ and PM_{10} concentrations monitored by the BPM (PM-monitor) are shown in Figure S2. High correlations (0.86 and 0.82) were observed.

Meteorological parameters, including wind speed (WS, m s^{-1}), wind direction (WD), temperature (T, ºC), relative humidity (RH, %), and pressure (P, Pa), were simultaneously monitored by the local Micro Meteorological Station (WS600−UMB, LUFFT, Germany).

2.3. ABB three−way receptor model

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

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

where x_{ijk} is the concentration of the jth component in the ith sample at the kth size; a_{ip} is associated with contribution pattern of the pth source to the ith sample; b_{jpk} is fraction

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

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

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

where C1 and C3 are user−specified parameters, which were 0.2 and 0.00002 in this work (Lee et al., 1999). The final contributions were calculated through the regression of PM mass concentration matrix and source contribution matrix.

When selecting variables, the variables with 1/3 data below DL were not used. If some components showed similar size distributions and temporal variations, and indicated consistent sources, sums of them were used. Thus, the following species were inputted for receptor modeling: Cl^-, NO_3^-, SO_4^{2-}, NH_4^+, Al, Ca, Ti, Fe, Cu, Na, K, Mn, Pb, OC1, OC2−4 (sum of OC2, OC3 and OC4), EC1, EC2−3 (sum of EC2 and EC3), three−ring PAHs (sum of Any, Ana, Flu, Phe, and Ant), four−ring PAHs (sum of Flt, Pyr, BaA and Chr), BbF, BkF, BaP, DBA, IPY, BghiP, Cor, C29αβ hopane, C30αβ hopane, C30ββ+C34αβR hopane, C15−18+C28 (sum of C15, C16, C17, C18 and C28 n−alkanes), C19−20 (sum of C19 and C20 n−alkanes), C23−26 (sum of C23, C24, C25 and C26 n−alkanes), and C31 n−alkane. Their full names are shown in Table S1. The

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

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

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

3. Results and discussion

3.1. Size-resolved chemical compositions

Concentrations of chemical species in the pseudo-ultrafine, fine and coarse modes during the four seasons are shown in Figure 1a and the reconstructions of chemical species are shown in Figure S5. The largest components were organic carbon fraction OC3, NO_3^-, and crustal elements (sum of Al, Ca, Fe and Ti) in the pseudo-ultrafine, fine and coarse modes, respectively. The size distributions (dC/dlogDp) of the main components are shown in Figure S6a. NO_3^-, SO_4^{2-} and NH_4^+ mass concentrations were

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

3.2. Size-segregated organic compounds

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

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

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

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

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

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

well as moderate OC2−4, crustal elements, K, Cor, C29αβ and C30αβ. The factor 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 moderate loadings of Cl^-, carbon fractions, crustal elements and four−ring PAHs. This factor profile is similar to the source profiles of coal combustion, characterized by carbon fractions, crustal elements and Cl^- (Bi et al., 2019). Cl^- was found in this factor since emissions of HCl from coal and biomass combustion can form semi−volatile ammonium chloride (Pio and Harrison, 1987). The four−ring PAHs, C15−18 n−alkanes and hopane have also been reported as organic markers of coal combustion (Bi et al., 2008; Zhang et al, 2008). As discussed above, four−ring PAHs and C28 n−alkane are significantly enhanced during winter, suggesting that they are indicative of coal combustion due to heating in Tianjin and surrounding regions. Higher molecular weight n−alkanes (like C28 here) may be predominantly of a vascular plant wax origin entrapped in the coals (Oros and Simoneit, 2006). K or K^+, Cl^-, OC and three− and four−ring PAHs may also arise from biomass combustion (Hays et al., 2005; Shen et al., 2011), so this factor likely contains a contribution from biomass combustion. Large scale biomass combustion is prohibited in Tianjin, so biomass combustion may be not an important source. Thus, factor 1 is identified as coal and biomass combustion (CBC).

As shown in Figure 3, the CBC contributed 21%, 14% and 12% in the pseudo-ultrafine, fine and coarse modes, respectively. Previous studies (Tian et al., 2016; Wang et al., 2016) consistently reported that coal combustion contributed higher fractions in fine PM than in coarse PM in Beijing and Tianjin. According to Figure 4a, the size distribution of the CBC mass contributions (dC/dlogDp, μg m^{-3}) was bimodal, with

peaks at 0.43−1.1 μm and 5.8−9.0 μm.

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

3.3.2. Factor 2: coal combustion (CC)

Factor 2 is characterized by high C30ββ+C34αβR, four−ring PAHs and carbon fractions at sizes 1.1−5.8 μm (Figure 2b). C30ββ and C34αβR are regarded as markers of less mature coals, such as lignite and sub−bituminous coal combustion (Oros and Simoneit, 2000), so factor 2 is identified as the other coal combustion (CC). Its percentage contributions accounted for 2% in the pseudo-ultrafine and 4% in the fine and coarse modes (Figure 3), and its size distributions showed a strong peak at 3.3−5.8 μm (Figure 4b). This factor made relatively higher contributions during early November and early March, which were the beginning and end of the heating season.

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

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

3.3.3. Factor 3: gasoline vehicles (GV)

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

C23−26 n−alkanes, which were similar at sizes <0.43, 0.43−0.65, 0.65−1.1, 1.1−2.1, 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 (Figure 2c). It has been reported that gasoline vehicles emit heavier PAHs (Phuleria et al., 2006) and C25−C26 n−alkanes (Schauer et al., 1999 and 2002).

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

3.3.4. Factor 4: diesel vehicles (DV)

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

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

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

3.3.5. Factor 5: resuspended dust (RD)

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

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

(dC/dlogDp) of this factor was unimodal at 3.3−5.8 μm (Figure 4e). The resuspended dust contributions showed a clear temporal variation with high contributions in spring and summer (Figure S8). It contributed 29%, 36%, 18% and 12% of PM_{10} during spring, summer, autumn and winter, respectively. As shown in Figures S9, resuspended dust contributions were high when wind speeds were strong. Stronger winds improve the dispersion of PM, but also can result in the resuspension of dust. Dry surfaces and strong wind speeds and vegetation impacts during spring and summer can explain the higher contributions of this factor.

3.3.6. Factor 6: industrial emissions (IE)

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

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

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

3.3.7. Factor 7: nitrate (NI)

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

Factor 7 is characterized by high NO_3^- and NH_4^+ at sizes < 2.1 μm, as shown in Figure 2g. This factor is attributed to "nitrate" aerosol. Its contribution was high at sizes 0.43−2.1 μm and showed a strong peak at size 0.65−1.1 μm (Figure 4g), contributing 9%, 16% and 5% in the pseudo-ultrafine, fine and coarse modes (Figure 3). The mass concentrations of this factor were low during summer (Figure S8), due to the thermodynamic instability of ammonium nitrate.

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

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

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

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

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

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

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

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

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

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

3.4. Size−resolved source apportionment by EPA PMF 5.0: comparison with ABB results

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

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

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

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

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

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

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

4. Conclusions

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

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