Characteristics and sources of hourly elements in PM$_{10}$ and PM$_{2.5}$ during wintertime in Beijing

Pragati Rai $^a$, Markus Furger $^a$,*, Jay G. Slowik $^a$, Haobin Zhong $^b$, Yandong Tong $^a$, Liwei Wang $^a$, Jing Duan $^b$, Yifang Gu $^b$, Lu Qi $^a$, Ru-Jin Huang $^b$, Junji Cao $^b$, Urs Baltensperger $^a$, André S.H. Prévot $^a$, **

$^a$ Laboratory of Atmospheric Chemistry, Paul Scherrer Institute, 5232, Villigen, PSI, Switzerland
$^b$ Key Laboratory of Aerosol Chemistry and Physics, Institute of Earth Environment, Chinese Academy of Sciences, 710075, Xi’an, China

** Corresponding author.

Abstract

Characteristics and sources of ambient particle elements in urban Beijing were studied by hourly observations in two size fractions (PM$_{10}$ and PM$_{2.5}$) during November and December 2017 using an online multi-element analyzer. The reconstructed oxide concentrations of 24 elements (from Al to Pb) comprise an appreciable fraction of PM$_{10}$ and PM$_{2.5}$, accounting for 37% and 17%, respectively, on average. We demonstrate the benefit of using high-time-resolution chemical speciation data in achieving robust source apportionment of the total elemental PM$_{10}$ (PM$_{10}^{\text{el}}$) and elemental PM$_{2.5}$ (PM$_{2.5}^{\text{el}}$) mass using positive matrix factorization (PMF). Biomass burning, coal combustion, secondary sulfate, industry, non-exhaust traffic and dust were identified in both size fractions (with varying relative concentrations), which accounted on average for 4%, 12%, 5%, 2%, 14%, and 63%, respectively to the total PM$_{10}^{\text{el}}$, and 14%, 35%, 21%, 6%, 12% and 12%, respectively to the total PM$_{2.5}^{\text{el}}$. Biomass burning and coal combustion exhibited higher concentrations during haze episodes of the heating season. In contrast, secondary sulfate and industry contributed more to haze episodes during the non-heating season. The fractional contribution of dust was mostly high during clean days, while the fractional non-exhaust traffic emission contribution was similar throughout the measurement period. The non-exhaust traffic emissions contributed locally, while the remaining sources were dominated by neighboring areas. Furthermore, trajectory analysis showed that the origin of the industrial sources roughly agreed with the locations of the main point sources. Overall, this work provides detailed information on the characteristics of the elements during different haze events during heating and non-heating seasons.

© 2021 The Author(s). Published by Elsevier Ltd. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

1. Introduction

A number of epidemiological studies have suggested that exposure to particulate matter (PM) is associated with a substantial health risk (Dockery et al., 1993; Dockery, 2009). The size and chemical composition of PM have been recognized as important factors for particle toxicity. For instance, Kan et al. (2007) found significant associations of daily mortality with PM$_{2.5}$, while Samoli et al. (2008) estimated a 0.2%–0.6% increase in the daily mortality per 10 $\mu$g m$^{-3}$ increase in PM$_{10}$. Since PM$_{2.5}$ and PM$_{10}$ may come from diverse sources with different physico-chemical properties, their composition can provide crucial information related to the particle origin, its formation processes and its effects on human health. Among the chemical components of PM, elements are important, and some of them are harmful to human health and the environment (Gao et al., 2016b; Tan et al., 2016). For example, Co, As, Cr$^{VI}$, Pb, Cd, Se and Ni are considered as human carcinogens even in trace amounts (Mulware, 2013). Cu, Cr, Fe and V are found in several oxidation states, which can catalyze the generation of reactive oxygenated species (ROS), which have been associated with oxidative damage to proteins and DNA within cells. Moreover, elements originate from various emission sources, such as traffic, industry, coal/biomass burning and soil dust, and could be emitted in a broad size range. To mitigate the effects of air pollution, it is...
necessary to identify and allocate pollution sources.

Air pollution in Northern China has received great attention in recent years. The air quality severely deteriorates during haze events, influencing human health and climate (Xie et al., 2016). High concentrations of PM_{2.5} and haze stagnant meteorological conditions are major factors in haze formation, which can significantly reduce atmospheric visibility. This is particularly evident during the cold season due to increased energy consumption and adverse meteorological conditions. In recent years, the Chinese government has implemented many policies to address increased air pollution. While air quality has been significantly improved, it is still far from ideal for the population. Although many studies on PM_{2.5}-associated elements were conducted in Beijing (Wei et al., 1999; Gao et al., 2014; Tian et al., 2016), most were explored prior to the APPCAP (Atmospheric Pollution Prevention and Control Action Plan) coming into force in 2013 (Zhao et al., 2013). Further, the reliance of earlier studies on low time-resolution sampling likely interfered with the precise source apportionment (SA) due to undetected rapid changes in the atmosphere. A highly time-resolved and size-segregated elemental dataset, combined with meteorological data, is beneficial for SA studies (Visser et al., 2015; Zhou et al., 2018; Rai et al., 2020a) and can be used to pinpoint the source regions. SA studies based on online measured elemental data in Beijing are relatively scarce (Gao et al., 2016a; Peng et al., 2016; Li et al., 2017; Cui et al., 2019; Liu et al., 2019; Zhang et al., 2019; Yang et al., 2020).

Based on the above background, elements in PM_{10} and PM_{2.5} in urban Beijing were measured by an online X-ray fluorescence spectrometer with high time resolution of 1 h from November 6, 2017 to December 12, 2017, to identify the prevailing sources.

2. Method

2.1. Sampling site

Beijing is located on the northwestern edge of the Great North China Plain and surrounded by the Taihang Mountains in the west and the Yanshan Mountains in the north and northeast, approximately 100 and 50 km, respectively away from the urban region. The closest coast from Beijing city is Bohai Sea, which is 160 km away to the southeast.

The sampling site (40.00°N, 116.38°E) was established in Beijing on the roof (~20 m above ground level) of a laboratory building in the National Centre for Nanoscience and Technology (NCCNT), Chinese Academy of Sciences (CAS). Two main roads were situated at about 800 m to the south and west. The site is mostly surrounded by educational and commercial properties, as well as residential dwellings and could be regarded as a representative urban site influenced by a wide mixture of emission sources (Elser et al., 2016). A building is located ~30 m north of the sampling site, which interferes with and blocks the wind from this direction. The sampling site is not influenced by major industrial sources. However, two waste incineration plants (~20 km) are located to the north and southeast of the sampling site (Cui et al., 2020).

2.2. Instrumentation

Elements in PM_{10} and PM_{2.5} were measured by an Xact 625i Ambient Metals Monitor (Cooper Environmental Services LLC, Tigard, Oregon, USA) with 1-h time resolution. The Xact is a semi-continuous online instrument, which samples and subsequently analyzes elements using the non-destructive energy-dispersive X-ray fluorescence (XRF) method. Xact data quality has been assessed in a number of field studies, and good agreement was found between the Xact and 24-h filter based measurements (Furger et al., 2017; Tremper et al., 2018; Zhang et al., 2019). In our study the sampling line in the Xact was modified to alternate between PM_{10} and PM_{2.5} (Furger et al., 2020). Because of this alternating sampling method, there was a gap of 1 h between each subsequent sample of the same size range. An automated moveable Teflon filter tape is used in the monitor; sample air is drawn through a small spot on the tape at a constant flow rate of 16.7 L/min. After the collection period, the tape then advances into the X-ray excitation and analysis section of the monitor and the collected sample spot is analyzed. At the same time, the monitor initiates new PM sampling on a previously unexposed spot on the tape. The duration of sample collection at each spot is 1 h, except for the time 0:00–01:00 h, which is used for internal checks as outlined below. The Xact is calibrated using thin film standards for the individual elements, and the response reproducibility during calibration throughout the campaign was within ±6%. Automated energy alignment checks are performed every day at midnight for 15 min, using a dynamic rod for Nb and Cr, which is inserted into the analysis area followed by a 15-min upscale check (for Cd, Cr, Nb and Pb). For every event of sample analysis, the Xact included a measurement of Nb as an internal standard to automatically adjust the detector energy gain, which was stable within ±5% throughout the measurements.

The Xact was able quantitatively to detect 35 elements (Al, Si, P, S, Cl, K, Ca, Mg, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Rb, Sr, Y, Zr, Nb, Cs, In, Sn, Sb, Ba, Hg, Ti, Pb and Bi, plus Nb for quality assurance). However, some of the elements’ data points were below the minimum detection limit (MDL) of the instrument for certain periods of time. For this analysis, we discarded the elements that were below MdL in PM_{10} and PM_{2.5} > 80% of the time (see Section 2.3).

Measurements of non-refractory (NR) PM were performed using a high-resolution (2 min) long-time-of-flight aerosol mass spectrometer (PM_{2.5} L-ToF-AMS) from 31 October until 5 December in 2017, as discussed in detail in Tong et al. (2020). Volatile organic compounds (VOCs) were measured by a proton-transfer-reaction time-of-flight mass spectrometer (PTR-ToF-MS, Ionicon Analytik GmbH, Innsbruck, Austria) with 30 s time resolution from 20 November to 8 December in 2017, as described in detail in Wang et al. (2021). NOx (Thermo Scientific Model 42i NO–NO2–NO, 91 analyzer) was monitored at the same site. PM_{10} and PM_{2.5} total mass concentrations were measured at the nearest national monitoring network station in Haidian District (~2.5 km away from the sampling site). The meteorological parameters, including temperature (T), relative humidity (RH), wind speed (WS) and wind direction were obtained from a meteorology tower, located at the Institute of Atmospheric Physics, CAS (39.97°N, 116.37°E), which is ~5 km away from the sampling site.

2.3. Source apportionment with PMF

PMF is a factor analysis method (Paatero and Tapper, 1994), which represents the measured elemental time series into as a linear combination of chemical profiles and time series of factors related to atmospheric sources. The model operates by minimization of the quantity Q, defined as the sum of the squares of the error-weighted residuals of the model. In conventional PMF analyses, rotational ambiguity coupled with limited rotational controls can impede clean factor resolution. In contrast, the multilinear engine implementation (ME-2) (Paatero, 1999) enables efficient exploration of the entire solution space by utilizing the so-called a-value approach (Canonaco et al., 2013), where the results are directed towards environmentally meaningful solutions. Here, a priori information is introduced by fixing one or more anchor profiles and/or time series from previous campaigns/analyses with varying degrees of freedom. The degree of freedom is regulated with the a-value, which can vary between 0 and 1 (0 means no
was constrained in the present study with an factor from the coal combustion factor, the BBOA factor time series (Tong et al., 2020). Therefore, to separate the biomass burning correlation (factor including waste incineration. In both studies, K is used as a random seeds for 4
was mixed with the coal combustion factor. The time series of hourly PM10el and PM2.5el concentrations as projected on the radar: 1 means 100% deviation allowed; 1 means 100% deviation allowed. This approach was previously applied to elemental data sets for separating distinct sources (Rai et al., 2020b) and was shown to provide improved factor separation compared to conventional PMF.

The source finder (SoFi) (Canaceno et al., 2013) tool version 6.9 for Igor Pro (WaveMetrics Inc., Lake Oswego, OR) was used for PMF input preparation and result analysis. The inputs were prepared by excluding some specific elements for better SA results. A most common approach to include species in the PMF input depends on the percentage of data below detection limit. With this approach, 24 elements (Al, Si, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Ga, As, Se, Br, Rb, Sr, Sn, Ba and Pb) were included in the PMF input. In addition, Ge was also included in the PMF input due to an excellent correlation (R = 0.85) with Ga during the entire period and moderate correlation (R = 0.6–0.7) with Pb, Zn, Br and Cl during high-intensity plumes. The PMF input consists of 411 and 408 time points of 1 h each in PM10 and PM2.5, respectively. For hourly diurnal cycles, linear interpolation was applied between two subsequent data points for each PM size fraction separately. The uncertainty as well as down-weighting corresponding to each data point was calculated by the approach mentioned in (Rai et al., 2020a). In the present study, additional element specific uncertainty related to the PMF solution by performing bootstrap analysis via random

The input data sets for PMF were constructed in two ways due to the availability of size-segregated data: (1) single size only; (2) both sizes arranged row-wise (i.e., 819 rows of 25 elements). Although both input data sets were investigated separately, we found similar factor profiles and corresponding time series throughout the input data sets. Therefore, we focus the PMF analysis on method (2) in our study. This approach has demonstrated to improve the statistical PMF analysis, and yielded robust PMF solutions (Amato et al., 2009; Cesari et al., 2018). The final input matrix contained 25 elements and 819 time points. The number of factors selected was evaluated by: (1) the interpretability of the retrieved factors by using the external data time series and their correlation with the retrieved factors; (2) identification of plume-related events; (3) comparison of factor profile markers with existing studies in Beijing. In the first step, unconstrained PMF runs were investigated with different random seeds for 4–10 factors, with a 5-factor solution selected as the meaningful representation of the data with the above criterion. The resolved 5 factors were: coal combustion, secondary sulfate, industrial, non-exhaust traffic and dust. Unlike recent SA studies on Xact datasets in Beijing (Cui et al., 2019; Liu et al., 2019), a biomass burning factor was not identified in the unconstrained PMF analysis. However, Cui et al. (2019) reported a mixed biomass burning factor including waste incineration. In both studies, K is used as a tracer of the biomass burning factor. The absence of a biomass burning factor in the initial PMF analysis is probably due to strong correlation (R > 0.9) of K with coal combustion markers (Cl, Br, Pb, Zn), which the PMF model was not able to clearly separate. In contrast, the constrained PMF analysis on organic aerosols (OA) identified a biomass burning OA (BBOA) with strong contribution from fragments of levoglucosan, i.e., mass to charge ratios at 60 and 73 (Tong et al., 2020). Therefore, to separate the biomass burning factor from the coal combustion factor, the BBOA factor time series was constrained in the present study with an a-value of 0.1. For higher a-values (looser constraints), the biomass burning factor was mixed with the coal combustion factor. The final base case yielded 6 factors including biomass burning, coal combustion, secondary sulfate, industry, non-exhaust traffic and dust.

We assessed the stability and estimated the uncertainties of the PMF solution by performing bootstrap analysis via random resampling of the time series (Davison and Hinkley, 1997). A total of 1000 bootstrap runs were performed on a 6-factor solution, with the biomass burning factor time series constrained by the BBOA time series using random initialization of a-values between 0 and 0.5 with an increment of 0.1. The bootstrap solutions were classified as mixed or unmixed as discussed in previous studies (Stefenelli et al., 2019; Rai et al., 2020a; Tong et al., 2020). In the first step, a 6-factor PMF solution was selected as the base case. In the second step, a correlation matrix of the Pearson R values of the retrieved factor time series with those of the base case was constructed for each bootstrap run. The matrix was sorted such that the highest R-values appeared on the diagonal. In the third step, each diagonal R-value was evaluated to determine whether it was statistically higher than any other values of the correlation matrix by selecting a significance level p (ranging from 0.05 to 0.5 with a step of 0.05) from a t-test. The bootstrap runs that fail in this test are classified as mixed solutions. In total 570 runs were classified as unmixed solution out of 1000 bootstrap runs at a p-value of 0.1.

3. Results and discussion

3.1. Characteristics of PM10 and PM2.5 elemental composition

The time series of hourly PM10el and PM2.5el concentrations as well as total PM10 and PM2.5 are shown in Fig. 1a. The entire measurement period was divided into a non-heating (6–14 November) and a heating (15 November–12 December) seasons, as the official heating season always begins on 15 November. Furthermore, based on the hourly total PM2.5 concentrations, the following episodes were defined and highlighted in Fig. 1a: clean days (no color in background): PM2.5 ≤ 25 μg m⁻³, light haze (light blue background): 25 μg m⁻³ < PM2.5 ≤ 150 μg m⁻³, and severe haze (light red background): PM2.5 > 150 μg m⁻³. The same episodic classifications are discussed in Figs. 2 and 5. The average total PM2.5el concentration was 5.2 ± 5 μg m⁻³ and ranged from 0.46 to 263 μg m⁻³, and the total PM10el concentrations ranged from 2 to 62.8 μg m⁻³, with an average value of 18.1 ± 12.5 μg m⁻³. The reconstruction of the average mass concentrations as oxides of the measured elements yielded 9.1 μg m⁻³ in PM2.5 and 37.2 μg m⁻³ in PM10. The detailed calculation of the reconstructed mass is described in the Supplement. The correlation between the reconstructed and total PM mass concentrations in both size fractions is shown in Fig. 1b. On average, the reconstructed PM10el mass made up ~37% of the total PM10 mass (69.4 μg m⁻³). The reconstructed PM2.5el mass accounted for ~17% of the total PM2.5 mass (40.6 μg m⁻³), which was ~2 times higher than that in Shanghai (Chang et al., 2018). This reveals that elements comprise a substantial fraction of PM10 and PM2.5 in megacities like Beijing, which should not be considered as a trace amount of total PM mass. The average concentrations of elements varied substantially, ranging from 1.7 ng m⁻³ for Se to 6060 ng m⁻³ for Si in PM10 and 0.11 ng m⁻³ for V to 1841 ng m⁻³ for Cl in PM2.5 (Table S1). Cl and S were the predominant PM components in PM2.5, with 35% and 21%, respectively, while crustal elements (Al, Si, Ca, Fe, Ti) showed high concentrations in the coarse fraction (PM10–PM2.5). The fractional contributions of Zn, Pb, Cu, As, Ni, and Se were higher in PM2.5 than in the coarse fraction and contributed 2.4%, 0.62%, 0.25%, 0.1%, 0.02%, and 0.03%, respectively (Table S1). In contrast, Cr and Mn were dominant in the coarse fraction. The concentrations of Zn, Pb, Cu, As, Ni, Se, Cr and Mn in PM2.5el were decreased by factors of 2–5 in comparison to winter 2016 measurements in Beijing (Liu et al., 2019), which may reflect the strict control plan implemented by APPCAP and/or meteorological differences between the studies (i.e., frequency of meteorological conditions giving rise to haze). However, approximately 10% of As data in PM10 is still above US EPA recommended inhalation reference concentrations (RFC) for residential air (Rai et al., 2021).
Fig. 2 shows the mean of all events in PM2.5 for non-heating clean, heating clean, light haze non-heating, and light haze heating classifications, as well as individual severe haze events defined as severe haze 1 (6–7 November), severe haze 2 (20–21 November), and severe haze 3 (2–3 December). It can be seen that the concentrations of most elements increased during haze days.
and were depleted during clean days. That is because the more stagnant meteorological conditions during different haze days could inhibit both vertical and horizontal transport, and thus, the local emissions played a more dominant role. To understand the transition between haze and clean days, we investigated wind speed and wind direction. Haze days were associated with low wind speed (<1.5 m s\(^{-1}\)) mainly from the south or southwest, and terminated by the arrival of air masses with higher wind speed (>3 m s\(^{-1}\)) from the north or northwest (Tong et al., 2020). Another interesting feature is that the concentrations of Fe, Ba, Ni, Mn, Cr, Cu, Se, and S were enhanced during severe haze 1 compared to the severe haze 2 and 3 events, with intense enhancement for S, Se and Ni. In contrast, Sr, K, Pb, Zn, Br and Cl were enhanced in severe haze 2 and 3 events. The higher concentrations of elements such as K, Pb, Zn, Br and Cl during the heating season are generally associated with the increased coal consumption for domestic heating. Si, Ti, Sn and Ca, associated with dust (partially true for Sn), showed less depletion (<30%) compared to the remaining elements during clean days, resulting in a higher PM\(_{2.5}\)el/PM\(_{total}\) ratio (Table S2). The variation in elemental composition between non-heating, heating, clean and haze episodes indicated changes in sources and/or chemical processes.

### 3.2. PMF results

As noted above, we selected a 6-factor PMF solution as the best representation of the data. This solution is presented in Fig. 3 (factor profiles), Fig. 4 (factor time series), together with their respective estimated uncertainties, and in Fig. 5 (factor contributions in different haze and clean episodes). The tabular representation of Fig. 5 is shown in Table S3. In Fig. 3, the fractional composition represents the relative composition of each factor (factor mass normalized to 1), and the relative contribution is the mass-weighted contribution of each factor to a given element. These factors are interpreted as biomass burning, coal combustion, secondary sulfate, industry, non-exhaust traffic and dust. Below we discuss each factor separately.

**Biomass burning:** This factor contributes >20% to K, Cl and Sn, while the mass is dominated by Cl (53%), K (23%) and S (16%). Cl in Beijing is used as an indicator of residential biomass burning during winter (Yang et al., 2018; Luo et al., 2019). Similarly, biomass burning (including burning of residential and industrial biofuel, agricultural waste, municipal solid waste and wildfires) is a primary source of K as shown in many previous SA studies (Dall’Osto et al., 2013; Cui et al., 2019; Liu et al., 2019). However, the major source of K and Cl during winter in Beijing is coal combustion followed by biomass burning (Yu et al., 2018). The S/K ratio of 0.56 in this factor profile is close to the value of 0.50 for fresh emissions rather than 8 for aged emissions (Viana et al., 2013), which suggests that biomass burning represents a primary aerosol. The fresh biomass emission can be in the form of particulate chloride (KCl), which is known to occur in fresh smoke (Li et al., 2003). The biomass burning factor time series was episodic, with maximum concentrations of up to 7.8 µg m\(^{-3}\) during the haze event from 18 to 22 November (Fig. 4a). The mass of this factor was predominantly in PM\(_{2.5}\)el. This factor accounted for 14% in PM\(_{2.5}\)el and 4% in PM\(_{10}\)el (Fig. 4b). Interestingly, the relative contribution of this factor in PM\(_{2.5}\)el was >10% during the heating season episodes, while it was <10% during the non-heating season episodes (Fig. 5). This is probably due to increased usage of biomass fuels for domestic heating during the heating season, particularly in the rural and suburban areas.

**Coal combustion:** This factor accounts for a major fraction of Cl (76%), Br (60%), As (60%), Pb (60%), Se (45%), Zn (43%), Ge (32%) and K (25%). Moreover, Cl (75%) and K (11%) mostly explain the mass of this factor. As stated above in the biomass burning section, Cl and K are important tracers of coal combustion in Beijing especially during severe haze in winter (Yu et al., 2018, 2019; Zhang et al., 2019). Apart from Cl and K, domestic coal combustion is also the
Fig. 4. Time series of the PM$_{10\text{el}}$ (red color) and PM$_{2.5\text{el}}$ (blue color) sources along with various auxiliary variables. Grey color indicates the uncertainties (interquartile) of selected 570 bootstrap runs. (b) Mean relative contributions of PM$_{10\text{el}}$ and PM$_{2.5\text{el}}$ sources. WS is wind speed, WD is wind direction. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Fig. 5. Relative contributions (error bars: ± one standard deviation) of the 6 resolved PMF factors in PM$_{10\text{el}}$ and PM$_{2.5\text{el}}$ during heating and non-heating seasons under clean (PM$_{2.5}$$\leq$25 µg m$^{-3}$), light haze (25 µg m$^{-3}$$<$ PM$_{2.5}$$\leq$150 µg m$^{-3}$) and severe haze (PM$_{2.5}$$>$150 µg m$^{-3}$ including severe haze 1, severe haze 2 and severe haze 3) episodes.
major source of As, Pb, Se, Zn, Ge and Br in Beijing (Tian et al., 2015; Li et al., 2018; Zhang et al., 2018; Cui et al., 2019). Moreover, the ratio of K/Pb (8.74) in this factor profile is close to that observed in Baoding (8.75) (an industrial city in Hebei Province, in the southwest of Beijing) from residential coal combustion (Liu et al., 2017). In our study, coal combustion produced high contributions during the heating season when large amounts of coal are used with intensive domestic heating in Beijing (Fig. 4a). These observations are consistent with the pronounced enhancement in heating haze events shown by K, Pb, Zn, Br and Cl (Fig. 2). The time series of this factor follows the coal combustion organic aerosol (CCOA) factor in PM$_{2.5}$ (R = 0.84) shown by Tong et al. (2020) (Fig. 4a). The diurnal patterns of this factor coincide with CCOA, which reflects the domestic heating activities with significant enhancement during nighttime (Fig. S1b). The mean contribution was dominant in PM$_{2.5el}$ (35%), while it was 12% in PM$_{10el}$ (Fig. 4b). The contribution of coal combustion to PM$_{2.5el}$ ranged from 40 to 52% during heating haze episodes (Fig. 5), which is close to the value of 57% estimated during winter 2010 in Beijing (Liu et al., 2016).

**Secondary sulfate:** This factor is mostly composed of S (84% of the factor mass), but also comprises substantial contributions to Se (5%), and As (30%). As and Se, potentially released from coal-fired power plants during high-temperature combustion, may be emitted in the vapor phase and subsequently condense onto the fly ash surface as the emissions cool (Vejahati et al., 2010). Similar to As and Se, particulate S can be emitted directly from coal combustion or form by SO$_x$ oxidation during transport. Se has a similar removal rate to that of S (in the form of sulfate) and is thus used to trace in-cloud oxidation of SO$_2$ (Husain et al., 2004). The mean SO$_4^2-/Se$ ratio of 3053 in this study is within the range of 1800–10000 in winter Pakistan aerosol (Husain et al., 2004). The time series of this factor follows inorganic SO$_x$ from AMS measurements (Fig. 4a) as well as the more oxygenated organic aerosol in the aqueous phase (MO-OOA$_{aq}$) factor of OA, and is interpreted to be related to secondary aerosol formed by aqueous phase chemistry. This factor is predominantly found in the fine fraction. In addition, this factor showed the highest relative concentrations (65% of the PM$_{2.5el}$ mass) during the severe haze 1 event (Fig. 5). The average relative contribution of this factor was 21% in PM$_{2.5el}$ while it was 5% in PM$_{10el}$.

**Industry:** This factor profile shows high relative contributions of Ga (100%), Ge (68%), Mn (47%), Sn (45%), Zn (32%), Pb (30%), Rb (28%) and Ni (24%). However, Fe (42%) and K (20%) dominate the mass. Ga and Ge are in high demand due to their usage in electronic devices such as smartphones, optoelectronics, fiber optics and solar cells (Moskalyk, 2004). Both elements are recovered from by-products of Zn metal processing (Sahoo et al., 2016). Another source for both elements can be coal fly ash from coal-fired power plants (Dai et al., 2012). However, Ga was not correlated to any elements while Ge was moderately correlated (R = 0.5) to Cl, Br and Pb. Mn, Zn, K, Sn, Ni, Rb and Pb are related to municipal waste incineration and ferrous metal smelting industries in China (Chang et al., 2018; Li and Achal, 2020; Zhang et al., 2018). The Zn/Pb ratio (4.3) in this factor profile is over 2 times higher than the value of 1.85 in incinerator emissions (Zhang et al., 2018), suggesting that Zn had other sources, such as nonferrous smelters. Therefore, this factor could arise from municipal waste incineration and ferrous/nonferrous metal smelting. This factor time series is prevailing in both sizes (PM$_{10el}$ and PM$_{2.5el}$) (Fig. 4a), which is a typical indication for influences of one or more point sources close to the sampling site. The industrial sources contributed only 6% and 2% to PM$_{2.5el}$ and PM$_{10el}$, respectively (Fig. 4b), likely because major manufacturing industries have been relocated to outside Beijing, with only smaller industries remaining within the city.

**Non-exhaust traffic:** This factor contributes >60% to Ba, Zr, and Cu, while the factor mass is dominated by Ca (30%), Fe (24%) and Si (21%). The relative contributions of this factor to Ca, Fe, Cr, Ni, Sr, and Ti are also non-negligible (18–40%). Cu, Zr, Ba, and Fe are tracers of non-exhaust vehicle emission (Visser et al., 2015; Cui et al., 2019; Daellenbach et al., 2020; Rai et al., 2020a). Non-exhaust particles typically arise from abrasive sources from brake and tire wear as well as abrasion of the road surface. Cu is usually used as lubricant and friction material in brake linings to improve friction stability and to reduce vibrations (Pant and Harrison, 2015). Ba, Si and Ca are incorporated in brake lining to reduce manufacturing costs and improve manufacturability, and are used as fillers and abrasives to increase friction (Grigoratos and Martini, 2015). Ti and Sr have also been found in concentrations lower than 0.1 wt% in brake composition (Whiteley, 2011). Cr and Ni are derived from vehicle fuel combustion processes (Song and Gao, 2011; Li et al., 2017). High correlations with NO$_x$ (R = 0.87) and a traffic factor (R = 0.81), resolved from PMF analysis of VOCs, suggests a strong influence of vehicular emissions on the factor. Concentrations of this factor peak from 06:00 to 10:00, corresponding to the morning rush hour, and from 17:00 to 22:00 in the evening, corresponding to evening-night rush hour (Fig. 5). The average relative contribution of this factor was more or less the same in PM$_{2.5el}$ (12%) and PM$_{10el}$ (14%) (Fig. 4b), while the average mass contribution was ~4 times higher in PM$_{10el}$ than in PM$_{2.5el}$. The relative contribution was more or less the same during heating and non-heating seasons (Fig. 5), which is consistent with the influence of local traffic emissions.

**Dust:** The dust factor accounts for >60% of V, Si, Sr, Al, Ti, Ca and >20% of Rb, Fe, Zr, Ba, K, Ni, Cr, Mn and Rb, while the mass is dominated by Si (47%), Ca (23%), Fe (12%) and Al (11%). These elements have been used as markers for crustal dust/soil, consistent with the upper continental crust composition (Chen et al., 2016). Ca is considered a good marker of construction dust, soil dust, or road dust in Beijing (Gao et al., 2016a). The K/Ca, Fe/Ca and Mn/Ca mass ratios in this factor were 0.16, 0.52 and 0.01, respectively, which is in agreement with the abundance in soil (0.12–2.6), paved road dust (0.01–0.08) and construction dust (0.05–0.26) (Ho et al., 2003; Yu et al., 2018). Therefore, this factor represents resuspension of particles from soil dust, road dust and construction dust. This is further corroborated by its diurnal variation, which shows negligible variability throughout the day (Fig. S1f). The factor time series revealed interesting features during measurements with strong dominance in PM$_{10el}$ (Fig. 4a). High wind speeds (>6 m s$^{-1}$) from the northwest accompanied by sand dust or sand dust storms can transport high PM$_{10el}$ concentrations to Beijing, and were observed during transitions from haze to clean periods. This was particularly evident on 7 November, 21 November, 28 November and 10 December. The average relative contribution was the highest (63%) in PM$_{10el}$ (Fig. 4b) with >80% during clean days, regardless of non-heating and heating seasons (Fig. 5). The average relative contribution in PM$_{2.5el}$ was 12% with >36% during clean days and it was within 2.5%–14% during different haze episodes throughout the measurement.

3.3. Potential geographic origins by concentration-weighted trajectories (CWT)

PMF time series were coupled with back trajectories using CWT. This approach couples concentration data measured at a receptor site with back trajectories and helps to localize air parcels responsible for high concentrations measured at the receptor site. More details about CWT can be found in Hsu et al. (2003). 72-h back trajectories were calculated each 3 h with the HYSPLIT model (Stein et al., 2015), using 1° × 1° weekly Global Data Assimilation System (GDAS) files. In order to match the calculated back trajectories time
resolution, the factor time series were averaged to 3 h. An ending altitude of 100 m above ground level (a.g.l.) was chosen so that the back trajectories ended within the mixing layer. Trajectory and CWT calculations were performed in Igor Pro with the ZeFir package (Petit et al., 2017).

The CWT plots of the different source contributions resolved by the PMF model are presented in Fig. 6. Biomass burning and coal combustion were important sources in the southwestern provinces around Beijing, which include heavily polluted cities such as Baoding and Shijiazhuang (Fig. 6a and b). In addition, the northwestern area of Beijing (Inner Mongolia) was also a potential source region for the biomass burning factor. The CWT plot for coal combustion suggests that residential coal combustion could make a dominant contribution in Beijing during the severe pollution period when the air parcels were usually from the south-southwestern region, where a high density of farmers reside. Although the Chinese government has implemented control measures for residential coal combustion (e.g., replacement of traditional coal stoves by new stoves, bituminous coal by anthracite, and coal by electricity and natural gas), the implementation strength of the control measures is still very limited. Additionally, the promoted new stoves still have large smoke emissions due to the lack of clean combustion techniques, and the anthracite is not welcomed by farmers because of its low combustion rate relative to bituminous coal. The results suggest that the pollutants from biomass burning and coal combustion were mainly transported from the surrounding areas of Beijing, including some local emissions within Beijing suburban and rural areas. The secondary sulfate originated predominantly from the south, including Baoding, Shijiazhuang and Xingtai (Fig. 6c). Shijiazhuang includes several coal-fired power plants (Fig. S2). The southern potential source areas indicated that the regional influences were important for the secondary sulfate.
factor. The industrial emissions showed probable source regions in the southern (Baoding and Tianjin) and eastern (Tangshan) areas (Fig. 6d). These areas are heavily industrialized, including municipal solid waste incineration, pig iron and steel plants, nonferrous metal smelting, etc. The CWT plot of non-exhaust traffic emissions showed potential source areas surrounding the sampling site (Fig. 6e). Note that the CWT plots of non-exhaust traffic emissions may have high uncertainties because localized emissions are dominant. As shown in Fig. 6f, high dust concentration probabilities were noted for air arriving from the northwest of Beijing. Rather than local emission, regional transport under high wind speed from the northwest of Beijing played thus an important role for dust. Fig. 6g shows the back trajectories during the entire period color coded by the date. It depicts that the air masses around 6−7 November and 24−27 November arrived from the most polluted areas south of Beijing, while the other air masses were from the northern to western regions of Beijing. The overall air masses during the measurements explain rather low concentrations compared to other years when there were probably more southerly haze episodes lasting for more than 5 days (Xu et al., 2018; Zheng et al., 2019).

In summary, the CWT analysis indicates that the southwestern and southern domains were the high potential source regions for secondary aerosol, coal combustion, industrial emissions and biomass burning, while it was the northwestern domain for dust and to some extent biomass burning. Non-exhaust traffic emissions were mostly of local origin. For all factors except non-exhaust traffic, the potential source areas outside Beijing on a regional scale were important in this period. The strict control strategies for coal combustion were likely essential to improving air quality in Beijing. In the meantime, more control of biomass burning, waste incineration and precursors of secondary sources in surrounding areas are also needed to mitigate air pollution in Beijing.

4. Conclusions

High-time-resolution measurements of elements in PM_{10} and PM_{2.5} were conducted during a fall/winter campaign 2017 in Beijing. The characteristics and sources of the elements were identified during different haze and clean episodes in the non-heating and heating seasons. The reconstructed mass concentration of the oxides of the measured elements amounted to approximately 37% and 17% of the total PM_{10} and PM_{2.5} mass, respectively, which should not be considered as a minor fraction of total PM on a mass basis.

Six sources, i.e., biomass burning, coal combustion, secondary sulfate, industry (solid waste incineration and nonferrous metal smelting), non-exhaust traffic and dust were identified by PMF analysis. PMF results showed that coal combustion was predominant (40%−52%) to PM_{2.5el} in haze episodes during the heating period, while dust (>80%) in PM_{10el} became more important in clean periods. Considering the limitation of receptor models, which could not identify and quantify regional transport, the PMF was combined with the CWT to analyze the specific sources from different source regions in and around Beijing. The source regions of elemental sources in Beijing were classified in a way that non-exhaust traffic dominated as the local emission source, secondary sources for air masses from the south, coal combustion from the southwest, industrial from the south and east, dust from the northwest and biomass burning from the southwest and west including local emissions close to the site. The results suggest that source contributions of PM_{10el} and PM_{2.5el} in winter in Beijing could change significantly, along with the contribution and direction of regional transport. Furthermore, it has been shown that size dependence should also be considered, otherwise inefficient or ineffective regulatory priorities may result (Rai et al., 2021).

Data availability

Data related to this article are available at https://doi.org/10.5281/zenodo.4584586 (Rai and Furger, 2021).

Author contributions

Pragati Rai: Conceptualization, Methodology, Formal analysis, Investigation, Software, Data curation, Visualization, Writing — original draft, Writing — review & editing. Markus Furger: Conceptualization, Investigation, Methodology, Supervision, Project administration, Funding acquisition, Writing — review & editing. Jay G. Slowik: Conceptualization, Investigation, Methodology, Supervision, Writing — review & editing. Haobin Zhong: Investigation, Resources. Yandong Tong: Investigation, Formal analysis, Data curation, Resources. Liwei Wang: Formal analysis, Data curation, Resources. Ru-Jin Huang: Investigation, Resources. Junji Cao: Investigation, Resources. Lu Qi: Investigation, Resources. Andre S. H. Prevot: Conceptualization, Supervision, Funding acquisition, Writing — review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This study was funded by the Swiss National Science Foundation (SNSF) projects (grant numbers 200021_162448, 200021_169787 and BSSG0_155846), and by the Swiss Federal Office for the Environment (FOEN). We acknowledge the Sino-Swiss Science and Technology Cooperation (SSSTC) project HAZECHINA (grant number IZLCZ2_169986), the Sino-Swiss Cooperation on Air Pollution Source Apportionment for Better Air (grant number 7F-09802.01), the SDC Clean-Air-China Programme (grant number 7F-09802.01.03), and the National Science Foundation of China (grant number 21661132005). The authors also acknowledge the funding received by the EU Horizon 2020 Framework Programme via the ERA-PLANET and transnational project SMURBS (grant agreement no. 689443), and the Swiss State Secretariat for Education, Research and Innovation (SERI; contract no. 15.0329−1). We acknowledge Dr. Stephan Henne from Empa for his support and discussion of trajectory calculations and interpretation and Prof. Dr. Lenny Winkel from ETH Zurich for her assistance to secondary sulfate factor interpretation.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2021.116865.

References

Amato, F., Pandolfi, M., Escrig, A., Querol, X., Alastuey, A., Pey, J., Perez, N., Hopke, P.K., 2009. Quantifying road dust resuspension in urban environment by Multilinear Engine: a comparison with PMF2. Atmos. Environ. 43, 2770−2780. https://doi.org/10.1016/j.atmosenv.2009.02.039.

Canonaco, F., Crippa, M., Slowik, J.G., Baltensperger, U., Prévôt, A.S.H., 2013. SoFi, an IGOR-based interface for the efficient use of the generalized multilinear engine (ME-2) for the source apportionment: ME-2 application to aerosol mass
APHEA study. Environ. Health Perspect. 116, 1480–1486. https://doi.org/10.1289/ehp.11345.

Song, F., Gao, Y., 2011. Size distributions of trace elements associated with ambient particulate matter in the affinity of a major highway in the New Jersey—New York metropolitan area. Atmos. Environ. 45, 6714–6723. https://doi.org/10.1016/j.atmosenv.2011.08.031.

Stefenelli, G., Pospisilova, V., Lopez-Hilfiker, F.D., Daellenbach, K.R., Hüglin, C., Tong, Y., Baltensperger, U., Prévôt, A.S.H., Slowik, J.G., 2019. Organic aerosol source apportionment in Zurich using an extractive electrospray ionization time-of-flight mass spectrometer (EESI-TOF-MS) – part 1: biogenic influences and day-night chemistry in summer. Atmos. Chem. Phys. 19, 14825–14846. https://doi.org/10.5194/acp-19-14825-2019.

Stein, A.F., Draxler, R.R.,olph, G.D., Stunder, B.J.B., Cohen, M.D., Ngan, F., 2015. NOAA’s HYSPLIT atmospheric transport and dispersion modeling system. Bull. Am. Meteorol. Soc. 96, 2099–2117. https://doi.org/10.1175/bams-d-14-00101.1.

Tian, J., Duan, J., Zhen, N., He, K., Hao, J., 2016. Chemical characteristics and source of size-fractionated atmospheric particle in haze episode in Beijing. Atmos. Res. 167, 24–33. https://doi.org/10.1016/j.atmosres.2015.06.015.

Tian, H.Z., Zhu, C.Y., Gao, J.J., Cheng, K., Hao, J.M., Wang, K., Hua, S.B., Wang, Y., Zhou, J.R., 2015. Quantitative assessment of atmospheric emissions of toxic heavy metals from anthropogenic sources in China: historical trend, spatial distribution, uncertainties, and control policies. Atmos. Chem. Phys. 15, 10127–10147. https://doi.org/10.5194/acp-15-10127-2015.

Tian, S.L., Pan, Y.P., Wang, Y.S., 2016. Size-resolved source apportionment of particulate matter in urban Beijing during haze and non-haze episodes. Atmos. Chem. Phys. 16, 1–19. https://doi.org/10.5194/acp-16-1-2016.

Tong, Y., Pospisilova, V., Qi, L., Duan, J., Gu, Y., Kumar, V., Rai, P., Stefene, G., Wang, L., Wang, Y., Zhong, H., Baltensperger, U., Cao, J., Huang, R.-J., Prévôt, A.S.H., Slowik, J.G., 2020. Quantification of solid fuel combustion and aqueous chemistry contributions to secondary organic aerosol during wintertime haze events in Beijing. Atmos. Chem. Phys. Discuss. https://doi.org/10.5194/acp-2020-835 submitted for publication.

Tremp, A.H., Font, A., Priestman, M., Hamad, S.H., Chung, T.-C., Pribadi, A., Vejahati, F., Xu, Z., Gupta, R., 2021. Potassium: a tracer for solid fuel combustion and health risk assessment. PM2.5 in Shandong Province: source identification and health risk assessment. Sci. Total Environ. 621, 558–577. https://doi.org/10.1016/j.scitotenv.2017.11.029.

Zhao, P.S., Dong, F., He, D., Zhao, X.J., Qiao, J., Liu, H.Y., 2013. Characteristics of concentrations and chemical compositions for PM2.5 in the region of Beijing, Tianjin, and Hebei, China. Atmos. Chem. Phys. 13, 4641–4659. https://doi.org/10.5194/acp-13-4641-2013.

Zhang, J., Zhou, Z., Wang, Z., Yang, L., 2018. Abundance and origin of fine particulate chloride in continental China. Sci. Total Environ. 624, 1041–1051. https://doi.org/10.1016/j.scitotenv.2018.01.003.

Zhou, S., Davy, P.K., Huang, M., Duan, J., Wang, X., Fan, Q., Chang, M., Liu, Y., Chen, W., Xie, S., Aneelcet, T., Trompetter, W.J., 2018. High-resolution sampling and analysis of ambient particulate matter in the Pearl River Delta region of southern China: source apportionment and health risk implications. Atmos. Chem. Phys. 18, 2049–2064. https://doi.org/10.5194/acp-18-2049-2018.