Exploring the cause of PM$_{2.5}$ pollution episodes in a cold metropolis in China

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Abstract

Harbin, a cold metropolis of China, frequently endures fine particles (PM$_{2.5}$) pollution during its long heating seasons, which has almost become the main environmental issue. To better understand pollution causes, multifaceted factors including the meteorology conditions, secondary transformation, source apportionment and regional transportation, were analyzed based on the definition of three pollution levels and eight pollution episodes. The results showed that chemical species varied dynamically and followed similar trends to PM$_{2.5}$, and secondary organic carbon and nitrate played more significant driving roles in PM$_{2.5}$ as the pollution level increased. Five sources were apportioned using the positive matrix factorization model, and the order of importance for the entire study period was as follows: secondary aerosol, traffic emissions, biomass burning, mineral dust, and coal combustion. The PM$_{2.5}$ in Harbin is mainly affected by transportation in the Harbin-Changchun megalopolis and slightly affected by long-distance transmission from the northwestern region of Harbin. A pollution episode in the fall was quite significant, as it was characterized by long duration time and extremely high pollutant levels, and was most likely attributed to extensive emissions from biomass burning and enhanced secondary transformation. The pollution episodes in winter were characterized by enhanced heterogeneous reactions and weakened photochemical reactions, which were especially sensitive to synoptic variations, and most likely induced by high relative humidity (>60%), low wind speed (3 m/s), suppressed planetary boundary layer height (<200 m), and strengthened inversion layer under the control of high-pressure systems. Meanwhile, the episodes in spring were characterized by high proportions of mineral dust, chlorine, and potassium, which was mostly attributed to the prevailing dust events, stronger biomass burning activities, and favorable transportation under low-pressure systems.

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1. Introduction

As a cold metropolis in China, Harbin is strongly influenced by the Siberian high pressure and Arctic Vortex. However, it still frequently endures fine particulate matter (PM$_{2.5}$)-dominated haze pollution during the long heating season. PM$_{2.5}$ pollution here is not fully controlled as it has received limited attention. The available official data (Fig. S1) indicate that PM$_{2.5}$ is the primary air pollutant in Harbin. Although the mean annual concentration declined from 2014 to 2018 (2014: 71 μg/m$^3$, 2015: 69 μg/m$^3$, 2016: 51 μg/m$^3$, 2017: 57 μg/m$^3$, 2018: 40 μg/m$^3$), severe pollution still frequently occurs during each heating season, and even triggers the red haze alert. PM$_{2.5}$ has almost become the main environmental issue during the heating seasons with 45.03% pollution days, while the percentage of pollution days in the on-heating seasons is 6.56%. Furthermore, as a cold metropolis, Harbin has longer heating seasons (last for six months from 20-October to 20-April each year) than most northern cities in China. During the heating seasons, the complex emission systems coupled with adverse meteorological
conditions caused severe haze events that threaten public health in the region and may influence climate change across a larger area, such as East Asia and the Arctic, due to its unique geographical location. However, the attention received by haze pollution does not correspond to its severity and complexity. Therefore, haze pollution is being gradually alleviated, but is far from being controlled. Many studies concerning air pollution have been conducted in the tropical and subtropical cities of China, but paid limited attention has been paid to air pollution in the cold metropolises. Air pollution is a global problem that requires local solutions (Li et al., 2019). Therefore, a deeper exploration of the causes of high-density PM$_{2.5}$ pollution is urgently required here.

The causes of high PM$_{2.5}$ pollution could be quite complex, as abnormally high PM$_{2.5}$ can be affected by various factors, including adverse synoptic systems, complex emission systems, secondary transformation, and regional transmission. Haze pollution is the result of the over-accumulation of pollutants, and this process is difficult to reverse once the total amount of pollutants meets the atmospheric capacity threshold, or the atmospheric capacity decreases due to changes in the meteorological conditions (Cai et al., 2017). In the above process, excessive emissions and secondary transformation are the most important causes of haze pollution and have received much attention from domestic and international studies. Multiple primary emissions have been identified (Gao et al., 2018), and various unusual phenomena were also discovered during polluted episodes, such as heterogeneous transformation and hygroscopic growth under high relative humidity, the formation of a two-way feedback mechanism between PM$_{2.5}$ and the atmospheric boundary layer (Wang et al., 2014a, b, c; Wang et al., 2014a, b, c), and the synergistic and competitive conversion of SO$_2$ and NO$_x$ (He et al., 2015). However, agricultural waste is commonly burned in important agricultural regions in China (Wang et al., 2011a; Zhao et al., 2015). Moreover, agricultural waste is commonly burned in the area to reduce straw accumulation, correspondingly causing large amounts of air pollutants (Cao et al., 2016; Qin et al., 2014).

In this study, PM$_{2.5}$ samples were collected from the roof of the School of Environment Building (45°45'14"N, 126°40'54"E, approximately 15 m above the ground) in the second campus of the Harbin Institute of Technology, which is located in a mixed zone of commercial and residential buildings, and traffic, without any major fixed pollution sources. Therefore, this area represents the typical urban environment of Harbin. The samples were collected using high-volume air samplers, equipped with PM$_{2.5}$ fractionating inlets (Laoying, Qingdao, China) every five days typically, or continuously during haze episodes. Ambient air was drawn into the sampler an average flow rate of 1.05 m$^3$/min for 24 h (8:00 a.m. to 7:59 a.m. the next day), and particulate matter particles with aerodynamic diameters of < 2.5 μm (PM$_{2.5}$) were collected on 8 × 10-in Tissquartz filters (PALL, NY, U.S.). All filters were sterilized in a Muffle furnace at 480 °C for 5 h and then packed in aluminum foil and stored in a sealed bag until they were loaded into the filter cartridge. The PM$_{2.5}$ concentrations were estimated from the flow-through volume (approximately 1531 m$^3$ in 24h) and the filter net weight recorded at 0.1 mg accuracy. After sampling, the filters were stored at −20 °C until post-chemical analysis were conducted. We also collected gas pollutants data (SO$_2$, NO$_2$) from the local air quality monitoring station for further analysis.

### 2.2. Chemical analysis

Two discs with 47 mm diameter were punched from each quartz fiber filter. One was extracted with 20 ml ultrapure water for soluble ions measurement (K$^+$, Ca$^{2+}$, Na$^+$, Mg$^{2+}$, NH$_4^+$, Cl$^-$, NO$_3^-$, F$^-$ and SO$_4^{2-}$) by ion chromatograph (Dionex, Thermo scientific, Inc.U.S). Another was digested with 15 ml nitric acid (guaranteed reagent) in electric heating plate digestion system for elemental measurement, including V, Cr, Mn, Ni, Cu, As, Cd, Pb, Ba, Ga, Sr, Ti, Co, Se, Rb, Ag, Sn, Sb, Cs, Tl, Fe, Zn, using inductively coupled plasma mass spectrometry (ICP-MS, Thermo Fisher, Inc. US). Two reagents blank and one filter blanks were conducted in each run following the same procedures as samples. The detection limit of ions was 10–30 ng/ml with the uncertainties <5%, and the detection limits of the elements ranged from 0.01 to 1 ng/ml with error <5%.

A 0.544 cm$^2$ punch from each filter was used to measure organic carbon (OC) and elemental carbon (EC) by a Desert Research Institute (DRI) Model 2001 Thermal/Optical Carbon Analyzer (Atmoslytic Inc., Calabasas, CA) following the Instrument Monitoring of Protected Visual Environment thermal/optical reflectance protocol. The measuring range of TOR was from 0.05 to 750 μg C/cm$^2$ with the error less than 10%.

### 2. Materials and methods

#### 2.1. Site description and sampling

Harbin (125.4°–130.1° E, 44.0°–46.4° N) is a well-developed industrial and agricultural mega-city in the Northeast China Plain, with the highest inhabited latitude, lowest temperature (−37.7 °C), largest land area (10,200 km$^2$), and third largest registered population (5.5 million) among all provincial capitals in China (Chen et al., 2018). The climate of Harbin is mainly continental monsoon, with the lowest temperatures occurring in January. The northern part of Harbin is the XiaoXing’an Mountains, while the southeastern part is the branch hill of Zhangguangcai Ridge. The urban area of Harbin is mainly distributed in the three-ladder formed by the Songhua River, which runs through the central part of the city (see Fig. 1). The topographic features of this region can be classified as a typical valley landform. The region surrounding Harbin located has fertile land that has been intensively cultivated over the last 50 years. With the increases in the areas of rice paddies, the Northeast China Plain has become one of the most important agricultural regions in China (Wang et al., 2011a; Zhao et al., 2015). However, agricultural waste is commonly burned in the area to reduce straw accumulation, correspondingly causing large amounts of air pollutants (Cao et al., 2016; Qin et al., 2014).

In this study, PM$_{2.5}$ samples were collected from the roof of the School of Environment Building (45°45'14"N, 126°40'54"E, approximately 15 m above the ground) in the second campus of the Harbin Institute of Technology, which is located in a mixed zone of commercial and residential buildings, and traffic, without any major fixed pollution sources. Therefore, this area represents the typical urban environment of Harbin. The samples were collected using high-volume air samplers, equipped with PM$_{2.5}$ fractionating inlets (Laoying, Qingdao, China) every five days typically, or continuously during haze episodes. Ambient air was drawn into the sampler an average flow rate of 1.05 m$^3$/min for 24 h (8:00 a.m. to 7:59 a.m. the next day), and particulate matter particles with aerodynamic diameters of < 2.5 μm (PM$_{2.5}$) were collected on 8 × 10-in Tissquartz filters (PALL, NY, U.S.). All filters were sterilized in a Muffle furnace at 480 °C for 5 h and then packed in aluminum foil and stored in a sealed bag until they were loaded into the filter cartridge. The PM$_{2.5}$ concentrations were estimated from the flow-through volume (approximately 1531 m$^3$ in 24h) and the filter net weight recorded at 0.1 mg accuracy. After sampling, the filters were stored at −20 °C until post-chemical analysis were conducted. We also collected gas pollutants data (SO$_2$, NO$_2$) from the local air quality monitoring station for further analysis.
2.3. Chemical mass closure

PM$_{2.5}$ composed of 10 most abundant categories in this study: organic matter (OM), EC, SO$_4^{2-}$, NO$_3^-$, NH$_4^+$, Cl$^-$, K$^+$, other ions, trace element oxides (TEO), and mineral dust. The factor converting OC to OM has been considered to ranging from 1.4 to 2.2, this study adopted 1.8 as literature suggested in autumn and winter (Tao et al., 2014). The minimum ratios of OC/EC were taken as representative of the primary emission to calculate the secondary organic carbon (SOC) (Li et al., 2016; Zong et al., 2018).

Other ions including soluble ions measured in section 2.2 except SO$_4^{2-}$, NO$_3^-$, NH$_4^+$, Cl$^-$ and K$^+$. Mineral dust was calculated by Fe (Zong et al., 2018), TEO was calculated by an equation introduced (Li et al., 2016; Zong et al., 2018).

\[
\text{OM} = 1.8 \times \text{OC}
\]

\[
\text{SOC} = \text{OC} - \text{POC} = \text{OC} - \text{EC} \times (\text{OC}/\text{EC})_{\text{prim}}
\]

Mineral dust = Fe/0.04

\[
\text{TEO} = 1.3 \times (0.5 \times (\text{Sr} + \text{Ba} + \text{Mn} + \text{Co} + \text{Rb} + \text{Ni} + \text{V}) + (\text{Cu} + \text{Zn} + \text{Cd} + \text{Sn} + \text{Sb} + \text{Ti} + \text{Pb} + \text{As} + \text{Cs} + \text{Ga} + \text{Ag}))
\]

2.4. Source analysis

Qualitatively and quantitatively sources apportionment were conducted by enrichment factors (EFs) analysis and positive matrix factorization (PMF) analysis in this study. EFs analysis was used to qualitatively assessment elements enrichment by human activities, it could be defined as (Zoller et al., 1974):

\[
\text{EFs} = \frac{(C/C_0)_{\text{Aerosol}}}{(C/C_0)_{\text{Crustal}}}
\]

Where C refers to target elements, and C$_0$ is the reference elements. Detailed classification of enrichment levels and degrees are shown in Table S1. (C/C$_0$)$_{\text{Crustal}}$ in this study referenced from the background value in the soil in China. Generally, Fe, Al and Si can be utilized as reference elements because they were considered less affected by other metal elements or anthropogenic sources, and have relative stable chemical properties and content ratios in the earth’s crust (Owens et al., 2005; Kersten and Smedes, 2002; Zhang et al., 2009). In our study, due to the interference from the aluminum packaging and the quartz fiber substrate of the samples, Fe was selected as reference element.

PMF 5.0 provided by the US EPA is a multivariate factor analysis tool, which relying on physically significant assumptions, that concentrations at a receptor site are supported by the linear combinations of different source emissions (Gao et al., 2018; Wang et al., 2017; Lee et al., 1999). It can solve the problem of negative factor loadings/scores by integrating non-negativity constrained factor analysis, making factor loadings and scores more interpretable (Paatero et al., 2013) (Text S1). In this study PM$_{2.5}$, mass concentrations, OC, EC, ions (K$^+$, Ca$^{2+}$, Na$^+$, Mg$^{2+}$, NH$_4^+$, Cl$^-$, NO$_3^-$, F$^-$ and SO$_4^{2-}$) and elements (V, Cr, Mn, Ni, Cu, As, Cd, Pb, Ba, Ga, Sr, Ti, Co, Se, Rb, Ag, Sn, Sb, Cs, Ti, Fe and Zn) selected as source profiles were put into PMF to quantitatively assess the major source contributions.

2.5. HYSPIT and PSFC modeling

Hybrid single-particle Lagrangian integrated trajectory (HYSPIT version 4.0) model which is available on the National Oceanic and Atmospheric Administration Air Resource Laboratory website (www.arl.noaa.gov/ready/hysplit4.html), was used to generate backward trajectories during sampling period. In this study National Center for Environmental Prediction (NCEP) GDAS data (1° × 1°) was used to simulated 72-h backward air mass in every sampling day, started at 00:00, 06:00, 12:00 and 18:00 of local time. The arrival heights of the trajectories in this study was set as 500 m, this height was considered can effectively reduce the influence of ground surface friction and accurately reflect the characteristic of mean flow field below atmospheric boundary layer (Wang et al., 2009).

Potential source contribution function (PSCF) introduced by Ashbaugh et al. (1985) was used in this study to assess and potential source regions of PM$_{2.5}$ and main source factors given by PMF result. PSCF is a conditional probability function, and was used to characterize the spatial distribution of possible geophysical
source locations of trajectories calculated by HYSPLIT. The probability that any given cell \((ij)th\) cell of PSCF field can be defined by the given equation:

\[
PSCF_{ij} = m_{ij}/n_{ij}
\]

where \(n_{ij}\) represents the total number of endpoints that fall in the \((ij)th\) cell, and \(m_{ij}\) represents the number of endpoints-oriented PM\(_{2.5}\) concentration or contributions exceeding given threshold. Here we set the threshold of PM\(_{2.5}\) concentration and contributions as 75 \(\mu\)g/m\(^3\) and 0.75 respectively. The grid layer covered by the trajectories was divided into an array of 0.5\(^{\circ}\) \(\times\) 0.5\(^{\circ}\) cells size. In order to remove the uncertainties caused by endpoints (Bressi et al., 2014; Li et al., 2017; Zong et al., 2018), an arbitrary weight function \(W(n_{ij})\) shown as following was multiplied with the PSCF value:

\[
W_{ij} = \begin{cases} 
1.00 & 80 < n_{ij} \\
0.70 & 20 < n_{ij} \leq 80 \\
0.42 & 10 < n_{ij} \leq 20 \\
0.05 & < 10 
\end{cases}
\]

### 2.6. WRF simulation

Advanced Weather Research and Forecasting model (WRF) was designed as a numerical weather prediction mode with options for various physical processes, but can also be applied as a regional climate model (Chen et al., 2011). This study introduces WRF 3.9, and calculated wind speed (WS), wind direction (WD), temperature (T), relative humidity (RH), and the height of the planetary boundary layer (PBL), also simulated surface (wind field, temperature field, and constant pressure line in horizon profiles) and vertical weather maps (constant temperature line, water vapor concentration and PBL height in vertical profiles) across sampling site. Synoptic data and meteorological field calculated by the National Center for Environmental Prediction (NCEP) data (1° \(\times\) 1°) from the website (https://rda.ucar.edu/). These data are available for 00:00, 06:00, 12:00, and 18:00 UTC, and two-dimensional data assimilation technology was used.

### 3. Result and discussion

#### 3.1. Pollution characteristics of PM\(_{2.5}\) and its chemical species

The temporal variations in the PM\(_{2.5}\) mass concentration during the heating season are shown in Fig. 2. In this study, we defined haze episodes as days when the PM\(_{2.5}\) mass concentrations exceeded the National Ambient Air Quality (NAAQ) Grade II standard of 75 \(\mu\)g/m\(^3\) based on previous studies (Wang et al., 2014a, b, c; Zheng et al., 2016), and 85% of the samples taken in the heating season were collected on hazy days. We also defined three pollution levels based on the NAAQ standard (http://106.37.208.228:8082/): clean (C, PM\(_{2.5}\) \(\leq\) 75 \(\mu\)g/m\(^3\)), slightly polluted (SP, 75 < PM\(_{2.5}\) \(\leq\) 150 \(\mu\)g/m\(^3\)), and heavily polluted (HP, PM\(_{2.5}\) > 150 \(\mu\)g/m\(^3\)). As highly concentrated and long-lasted episodes are more harmful and receive more public attention, this study specially focused on heavily polluted episodes for detailed analysis, and further categorized one special pollution episode (SPE) and seven short-duration polluted episodes (PE1-PE7; Fig. 2). These episodes were characterized by a long duration or abnormally high PM\(_{2.5}\) mass concentrations (exceeding 150 \(\mu\)g/m\(^3\)), and were selected to explore the causes of haze during the heating season in Harbin. Consecutive heavily polluted samples were merged into one episode. The concentration of PM\(_{2.5}\) in the study period ranged from 33.17 to 765.61 \(\mu\)g/m\(^3\) and fluctuated significantly. SPE occurred in late October and early November, beginning on October 25. Three peak values occurred on October 27 (411.43 \(\mu\)g/m\(^3\)), November 1 (554.93 \(\mu\)g/m\(^3\)), and November 6 (765.61 \(\mu\)g/m\(^3\)), and the event then dissipated on November 7. PE1 (PE1-EP7) occurred alternatively with clean days from December to April and were characterized by relatively lower PM\(_{2.5}\) mass concentrations and a shorter duration time than SPE, only two episodes with PM\(_{2.5}\) concentrations exceeding than 250 \(\mu\)g/m\(^3\) occurred, which were on January 1 and April 5.

The time series of chemical species exhibited a similar temporal trend to PM\(_{2.5}\), with elevated concentrations during polluted episodes and the highest concentration occurring during the SPE (Fig. 2). Carbonaceous components were the most abundant species and strongly correlated with PM\(_{2.5}\) (r\(_{OC}\) = 0.878, r\(_{EC}\) = 0.788, Fig. S4), with average concentrations of 29.18 and 7.89 \(\mu\)g/m\(^3\) throughout the observation period, indicating that they predominantly contributed to PM\(_{2.5}\) pollution. Among the water-soluble ions, NO\(_3\) was the most abundant, with an average concentration of 8.45 \(\mu\)g/m\(^3\), followed by SO\(_4^{2-}\), Cl\(^-\), NH\(_4\)\(^+\), and K\(^+\), with average values of 6.19, 5.93, 5.66 and 3.11 \(\mu\)g/m\(^3\) respectively. The concentrations of other ions (Ca\(^{2+}\), Na\(^+\), Mg\(^{2+}\), F\(^-\)) were low. The fraction of secondary inorganic (SNA, sulfate, nitrate and ammonium) (below 19.74%) in this study was not predominant, as was observed in previous studies (25.4%–46.49%) (Zong et al., 2018; Li et al., 2017), but was still the second-most predominant component. In this study, NO\(_3\) accounted for the largest part of the SNA (Figs. 2–3), and its content sharply increased during SPE and PE1-PE3. The SO\(_4^{2-}\) concentration was relatively stable, and generally exceeded that of NO\(_3\) on clean days. The NO\(_3\)/SO\(_4^{2-}\) mass ratio has been widely used as an indicator of the relative importance of mobile and stationary sources of nitrogen and sulfur in the atmosphere. Higher (8–13) NO\(_3\)/SO\(_4^{2-}\) ratios are typically associated with emissions from gasoline, diesel fuel, or biomass burning (Wang et al., 2006; Cao et al., 2016), while lower ratios (0.27–1.0) are typically associated with coal-burning (G. Wang et al., 2015; Q. Wang et al., 2015). In this study, the NO\(_3\)/SO\(_4^{2-}\) ratio was generally below 1.0 on clean days, and gradually increased as the pollution level increased, indicating that the drivers of PM\(_{2.5}\) formation shifted from coal combustion on clean days to traffic or biomass burning on polluted days, which was also observed in studies conducted in Shanghai and Chengdu (Li et al., 2017; Wang et al., 2006). The more prominent role of NO\(_3\) in haze formation may due to the continuously increasing car ownership and promotion of boiler desulfurization. The properties of Cl\(^-\) and K\(^+\) observed in this study were higher than those observed in previous days (Tao et al., 2014; Zhang et al., 2013; Gao et al., 2018; Zong et al., 2018), and the PM\(_{2.5}\) concentration was more closely correlated with Cl\(^-\) (r = 0.846) and K\(^+\) (r = 0.833) than NO\(_3\) (r = 0.787) and SO\(_4^{2-}\) (r = 0.763) (Fig. S4). The contents of potassium and chlorine in aerosols from biomass burning are enriched, and fresh biomass-burning plumes are generally characterized by high potassium chloride contents, while aged biomass burning smoke contains high amounts of potassium sulfate/nitrate (Cao et al., 2016). The stronger relationship (r = 0.935, Fig. S4) between potassium and chloride in our study than that of sulfate/nitrate clearly demonstrated that the biomass aerosol likely originated from local emissions. Furthermore, the higher contents of chloride and potassium observed in SPE, PE4, PE5, and PE6 also corresponded to densely distributed fire points in the Harbin-Changchun megalopolis (Fig. S3). As indicated by the chemical composition of PM\(_{2.5}\) presented in Fig. 3, the content of OM was remarkably high, with a maximum proportion of 35.93% in all categories, followed by mineral dust, NO\(_3\), EC, SO\(_4^{2-}\), Cl\(^-\), NH\(_4\)\(^+\), K\(^+\), other ions, and TEO. As the pollution...
level increased, the fractions of SOC and NO$_3^-$ increased sharply, those of NH$_4^+$, Cl$^-$ and K$^+$ fraction increased slightly, while the proportions of primary organic carbon (POC), EC, SO$_4^{2-}$, mineral dust, and TEO decreased. The substances with increased proportions may play more important roles in pollution formation (Zheng et al., 2016), and strong positive correlations were observed between them (Fig. S4), indicating that they likely originated from common sources. In SPE, EP1, EP2 and EP3, carbonaceous components and SNA were observed accounting at high proportions (50.82%–62.12%), these episodes were closely related to the secondary reactions and can be defined as pure-haze. However, EP4–EP7 were driven by mineral dust and can be defined as mixed haze-dust. During SPE, EP5, and EP6, the concentration of K$^+$ and Cl$^-$ were extremely enhanced and may have been significantly influenced by biomass burning.
3.2. Influence of synoptic weather system

The dynamic variations in the PM$_{2.5}$ mass concentration during the heating season could be partly induced by the unfavorable diffusion conditions, which are reflected by the meteorological parameters, such as PBL, WS, WD, T, and RH (Ning et al., 2018). The PBL was mostly below 500 m from November to March, and below 200 m during heavily polluted episodes (SPE, PE1-PE4), but higher in April. As shown in Fig. 4, the influence of PBL on PM$_{2.5}$ followed two different influence mechanisms. Contrasting trends between the PM$_{2.5}$ concentration and PBL were observed when the PBL height was below 500 m, and synchronized trends were observed when the PBL height was above 500 m. Westerly winds were predominant throughout the study period; WS fluctuated around an average value of 3.47 m/s and was positively correlated with the PBL height, with a correlation coefficient of 0.481 (Fig. S4). The WS in EP1-EP3 were below 3 m/s, but exceeded 3 m/s during the other episodes. The temperature decreased from October to January, and then increased, following an opposite trend to the RH. The Siberian high pressure is the main factor affecting the temperature in Northeast China during winter (Zhang et al., 2016). In this study, temperature was strongly correlated with PBL ($r = 0.617$) but negatively correlated with RH ($r = -0.44$). Therefore, the Siberian high pressure was likely the main cause of the low PBL, low temperature and high RH from November to March. The abnormally high pressure was likely the main cause of the low PBL, low temperature inversion layer acted as a lid to suppress vertical diffusion, while the low surface wind-speed favored the accumulation of pollutants along the horizontal scale. High RH, enhanced stability and transiently rebounded temperature could initiate a series of chemical chain reactions (Wang et al., 2014a, b, c).

To explore the physical vertical mixing and horizontal dispersion mechanisms involved in the formation of SPE and PEs, surface weather maps (Fig. 4) and west-east vertical profiles (Fig. 5) were drawn for each type of episodes. The surface weather maps for polluted episodes were generally categorized into two types: high-pressure system-governed and low-pressure system-governed episodes. During the SPE, a low-pressure system initially formed, accompanied by the first peak value on October 27. In the subsequent days, a high-pressure system developed along with extremely high PM$_{2.5}$ concentrations on November 1 and 6. The SPE eventually dissipated on November 7, when the region was controlled by a low-pressure system again. In the PEs, the sampling site was successively governed by low-pressure centers (Fig. 5: EP1 (1), EP3, EP4), high-pressure ridges (Fig. 5: EP1 (2), EP2), and low-pressure troughs (Fig. 5: EPS-EP7). The west–east vertical profiles of temperature and the RH crossing the sampling site were analyzed to investigate the vertical exchange capacity, and adverse vertical weather systems with low PBL, temperature inversion, and high RH were observed during SPE and EP1–EP4 which were mainly governed by a high-pressure system (Fig. 6). Low-pressure system-governed episodes (EPS-EP6) conversely corresponded to high PBL, steep temperature stratification, and low RH in the vertical profiles (Fig. 6).

In summary, the synoptic weather system from November to March was generally controlled by the Siberian high-pressure, which decreased the PBL height and surface temperature, increased the RH, and suppressed the diffusion system. When high-pressure systems reached the sampling site, the surface wind speed was reduced while the stability was enhanced, and unfavorable diffusion conditions was further strengthened (PE1-PE4). High-pressure systems can promote strong air mass-sinking motions (Seo et al., 2017; Zhang et al., 2016), suppress the PBL height, induce humid and warm advection, and strengthen the inversion layer. The developed temperature inversion layer acted as a lid to suppress vertical diffusion, while the low surface wind-speed favored the accumulation of pollutants along the horizontal scale. High RH, enhanced stability and transiently rebounded temperature could initiate a series of chemical chain reactions (Wang et al., 2014a, b, c). However, the weather patterns before November 1 and after March
30 were generally characterized by a low-pressure system, sharp temperature gradient, strong wind, and low RH, which were all conducive to effective regional pollution transport. Previous studies also demonstrated that sand or floating dust caused by cyclonic activity and the thawed land surface could also be a major cause of the deteriorated air quality in Northern China during spring.

3.3. Role of secondary aerosol transformation in high density PM$_{2.5}$ pollution

Recent studies reported that secondary aerosols drive haze formation in China (Seo et al., 2017; Zheng et al., 2016). To explore the underlying mechanism, this study conducted further episode-based analysis of SOC, OC/EC, sulfur oxidation ratios (SOR) and Nitrogen oxidation ratios (NOR). OC is generally composed of POC and SOC, while EC is primarily derived from the incomplete combustion of carbon-containing materials (Zong et al., 2018). SOC is catalyzed by crucial oxidants, such as O$_3$ and OH, in photochemistry production and aerosol-aging (Jimenez et al., 2009; Hallquist et al., 2009), while the OC/EC ratio can eliminate the physical variations of mixing/dilution and be used to better evaluate the contribution of secondary organic chemical reactions (Zheng et al., 2015). In this study, the OC/EC ratio was strongly correlated with SOC ($r = 0.907$), suggesting that it can be used as an indicator of secondary reactions. SOR and NOR (SOR = nSO$_4^{2-}$/[nSO$_4^{2-}$ + nSO$_2$ in mol], NOR = nNO$_3^{-}$/[nNO$_3^{-}$ + nNO$_2$, in mol]) are usually calculated to indicate the secondary conversion efficiency of atmospheric sulfur and nitrogen, and it has been reported that the content of SOR in the primary source emissions was below 0.10 (Pearson, 1979; Truex et al., 1980), while it exceeded 0.10 when sulfate was produced through the photochemical oxidation of SO$_2$ (Ohta and Okita, 1990; Zheng et al., 2016; Li et al., 2017). Higher values of SOR and NOR indicated extensive secondary oxidation reactions, and lower values were considered to indicate primary source emissions (Sun et al., 2006; Pearson, 1979). The higher OC/EC ratios, estimated SOC fraction, SOR, and NOR along with higher pollution, suggested that photochemistry and heterogeneous chemistry were enhanced during the heating season (Table S2).

The SOC concentration and OC/EC ratio in HP were higher than those in SP, and extremely enhanced in SPE, EP5, and EP6, which increased their average value in HP and indicated reduced photochemistry and aerosol-aging during other pollution episodes. However, the SOC fraction was not increased in all PEs, and significantly lower values than those on polluted days and clean
days were observed during PE1-PE4 and PE7, suggesting a weakened photochemical reaction. This study attempted to explore the underlying reason for this based on meteorological parameters (Fig. S4), and the results showed that SOC and OC were positively correlated with temperature and PBL, and negatively correlated with RH. As discussed above, the sampling site experienced a high-pressure system during PE1-PE3, and the sinking airflow decreased the PBL height, weakened vertical mixing and aggravated the accumulation of pollutants. Owing to the strong radiation effect of the accumulated particles, the solar radiation intensity and photolysis reaction were weakened, which is important in the production of radicals and near-surface ozone, and eventually inhibited the formation of SOC. The enhanced secondary organic reaction in SPE, EP5 and EP6 corresponded well with the densely distributed fire points as supported by the fire maps (Fig. S3). Furthermore, the PBL in these episodes was relatively high (Fig. 4), and the large amount of aerosol of released organic aerosol together with the strong radiation intensity tremendously promoted the photochemical reactions and SOC formation. Therefore, the photochemical reactions were directly affected by the radiation intensity and oxidant concentration (Ozone (O₃) and Hydroxyl radicals (OH)), which was also observed for haze in Beijing (Zheng et al., 2015; Li et al., 2017). During the SPE and PE1-PE3, the high NOR values were most likely linked to the heterogeneous reactions with O₂ under the catalysis with a transition metal due to weakened photolysis. Additionally, ammonium was closely related to RH (0.647), sulfate (0.739), nitrate (0.658), and NOR (0.624). As the main alkaline component of SNA, ammonium plays an important role in neutralizing H₂SO₄ and HNO₃, while promoting NOR and SNA formation. With the onset of the aqueous phase due to the high RH (>60%), the heterogeneous reactions were enhanced in the SPE, and EP1-EP3, resulting in the rapid accumulation of SAN (14.37%–19.74%; Fig. 3, Table S2). The predominant roles of RH, aerosol liquid water content and aerosol acidity in the heterogeneous oxidation of fine particle explosive growth events were also profoundly demonstrated by the online observation in Beijing (Liu et al., 2017, 2019). The secondary reaction was highly complex in EP4-EP7 due to the occasionally enhanced/weakened photochemical and heterogeneous reactions; however, there is no clear cause can be extracted. Multiple factors may have been responsible, including volatile weather systems.
Stronger biomass burning activities and frequent dust events.

### 3.4. Source apportionment

The total concentration of the analyzed inorganic elements was 2.59 µg/m³, which was only 1.58% of the total PM₂.⁵ mass concentration. These elements constitute a minor fraction, but are important tracers in atmospheric environments (Chang et al., 2017). The concentration of Fe was highest among all trace metals, with a proportion of 32.23%, and its concentration was highest in spring, manifesting great contributions from crustal dust. To evaluate the contamination degree of inorganic elements and determine whether they originated anthropogenic or natural sources, the enrichment factors (EFs) were calculated (Fig. 7). The EF values of Ti, Rb, V, Cs, Ba, Co, Mn, and Sr were below 10, and their concentrations were high in spring and autumn but low in winter. This suggests that there was almost no enrichment from anthropogenic sources, and these elements can be used as tracers of mineral dust. The EF values of Ni, Ti, Cr, Ag, Zn, Sn, As, Pb, Cu, Sb and Cd exceeded 10, indicating that they were strongly enriched by anthropogenic sources.

This study used PMF version 5.0 to identify the potential sources of PM₂.⁵ (biomass burning, vehicle emission, biomass burning, mineral dust, and secondary aerosols) and estimate their contributions based on above analysis. The PMF model was run 100 times, and most residuals were between -3 and 3. The coefficients of determination for the observed and predicted values (r²) mostly exceeded 0.6, indicating that the model was reasonable for explaining the information contained in the original data. The modeled source profiles and percentage contributions are shown in Fig. 8(a). The first factor interpreted low proportions of carbonaceous materials and SNA, but high proportions of crust tracer, such as Sr, Fe, Al, and Ba according to the EFs analysis and Na⁺, and its normalized source contributions remained near 0 before January, but gradually increased and eventually peaked during March and April (Fig. S3), which agreed well with the prevalence of dust events in northern China during spring. Therefore, this source was identified as mineral dust. The second source was identified as biomass burning due to the relatively high proportions of OC and EC, and extremely high proportions of plant components, such as K⁺, Cl⁻, F⁻ and Mg²⁺. The contribution of the second source during fall and spring were significantly and slightly elevated, respectively, which corresponded well with the burning of agricultural waste as indicated by the fire maps (Fig. S3). As it is one of the most productive agricultural regions of China, agricultural waste is commonly burned in this region, which is the main cause of the occurrence of severe haze after harvesting and before sowing (Wang et al., 2011; Qin et al., 2014). The third source is traffic emissions, which are strongly enriched with heavy metals, such as Cr, Mn, Cu and Ga, and crustal tracers, such as V, Ba, Cs, Rb and Fe. V is usually used as an additive in lubricating oil and enters the atmosphere through tailpipe emissions. Cu, Mn, Ga, Ti, and Cr are used in catalytic converters, tire manufacturing, and brake linings, and Ba, Cs, Rb and Fe are mainly contained in fugitive dust (Han et al., 2017; Chang et al., 2017; Lin et al., 2015). The normalized concentration of this factor fluctuated stably and was consistent with the vehicle pollution characteristics. The fourth factor was characterized by high proportions of EC, SO₄²⁻, As, Pb, Co, Ga, Ag, Sn, Sb, Ti, and Zn, and was consistent with the emission features of coal combustion. The contribution of this source first increased and then decreased, following an opposite trend to temperature, and the variations in the contribution were consistent with the demand of residential coal burning under low-temperature conditions. The final source is secondary aerosol owning to the significantly high proportions of OC, SO₄²⁻, NO₃⁻, and NH₄⁺. The contribution of secondary aerosols was higher in SPE, PE1-PE3, and PEs, which was consistent with the secondary aerosol transformation analysis above. High contributions of secondary aerosol to PM₂.⁵ have been observed in many studies conducted in China, such as Jing-Jin-Ji (9.0%–61.6%) and Chengdu (33%–44%; Table S3).

Secondary aerosol (32.30%) played the most important role in PM₂.⁵ pollution during the heating season, followed by traffic emissions (23.90%) and biomass burning (23.30%), while coal combustion (6.2%) and mineral dust (14.4%) were small contributors. The contributions of different sources to the PM₂.⁵ mass concentration under different pollution levels are shown in Fig. 8(b). Secondary aerosol formation contributed the most to the rapid accumulation of PM₂.⁵ during polluted episodes, accounting for 41.40%, and 38.2% in the SPE and PEs respectively. Biomass burning was the fundamental cause of SPE, while traffic emission (24.90%), coal combustion (16.10%) and mineral dust (13.20%) combined with unfavorable weather conditions collectively caused the PEs. As indicated by the analysis above, the emissions from coal combustion and vehicles fluctuated regularly during the heating season, and the PEs occurred irregularly to the unfavorable synoptic weather. Traffic emissions and biomass burning were identified as...
major factors by the PMF model, which offered new insights to alleviate PM$_{2.5}$ pollution. Preventing straw burning could significantly reduce the occurrence of pollution episodes during autumn and spring. Additionally, further managing traffic pollution could also be effective. Therefore, clean energy vehicles and improved gasoline should be widely implemented in the public transportation system.

3.5. Regional transportation

Regional transportation was found to contribute considerably to the rapid accumulation of PM$_{2.5}$. Therefore, the trajectories of the air masses and potential geographical origins were analyzed to explore its influence. Fig. 9 shows the 72-h backward trajectories of air masses, trajectory clusters, and the potential geographical origins during the heating season. On the sampling days, the air masses mostly originated over Russian and Mongolia, which experienced fast-moving and long-distance transmissions before reaching the sampling site. Based on the trajectory routes, four clusters were identified which all originated from the northwest. This suggests that the Siberian high-pressure and strong prevailing northwesterly winds were predominant during the heating season. The air parcels during the SPE mostly originated from the northwestern region and passed through the Harbin-Changchun megalopolis (Fig. S2), and some originated from the North China Plain. Severe haze was monitored in other cities of the region at the same time (Table S4), which likely contributed to the rapid accumulation of PM$_{2.5}$. During the PEs, the air masses mainly originated from the northwestern regions of Harbin, and likely carried pollutants from the Harbin-Changchun megalopolis (Fig. S2), as indicated by the monitoring data (Fig. S4).

To determine the potential geographical origins of PM$_{2.5}$ and the source factors given by the PMF model, this study conducted PSCF analysis based on the HYSPLIT model, and the possible geographical origins were indicated in different colors. Regions that were highly likely to be sources of PM$_{2.5}$ (>0.3) were mainly located in the Harbin-Changchun megalopolis, and were also sporadically distributed in farther regions, such as the North China Plain and the border of Inner Mongolia and Russian. Therefore, the PM$_{2.5}$ in Harbin was mainly affected by local emissions and slightly affected by long-distance transmission. The potential geographical origins of the source factors were similar to those of PM$_{2.5}$, but with different probabilities. The probabilities of biomass burning and secondary aerosol being origins were lower than those of the other...
factors in lighter colors, reflecting weaker transport of their emissions. The coal combustion and traffic emission sources were stronger than the other factors, and the pollutants received by the sampling site likely had a remote source. Traffic emission sources were densely distributed in the Harbin-Changchun megalopolis, which has heavily used roads, while coal combustion sources were scattered across large regions where coal-fired plants may have existed. The mineral dust sources were distributed in remote areas, but were as the local sources, which was consistent with the distribution of natural sources. In conclusion, the PM$_{2.5}$ in Harbin was mainly affected by regional transportation from the Harbin-Changchun megalopolis and long-distance transmission from the northwestern region. Biomass burning and secondary aerosol were slightly affected by regional transportation, while traffic emissions, coal combustion, and mineral dust were severely affected. According to Fig. 9, traffic emissions were densely distributed in the Harbin-Changchun megalopolis, while coal combustion and mineral dust were scattered across large scale regions, which was consistent with their distribution features. Based on the above analysis, regional pollutant emissions should be mitigated and prevented by different regions and cities, and at various levels of the government.

4. Conclusion

Several factors were analyzed in Harbin during heating season to elucidate the causes of the formation of high PM$_{2.5}$ mass concentrations from four aspects, i.e., synoptic weather, secondary transformation, source apportionment, and regional transportation. The major conclusions are as follows:

During the heating season, the level of PM$_{2.5}$ varied dynamically, and its concentration exceeded 75 $\mu$g/m$^3$ in 85% of the samples. Three pollution levels (C, SP, and HP) and 8 polluted episodes (SPE, PE1-PE7) were defined based on the NAAQ standard. The time series of the chemical species exhibited a similar trend to the variations in the PM$_{2.5}$ concentration, and their concentrations were mainly elevated in pollution episodes. Among all species, the concentration of OM was highest, followed by NO$_3^-$, EC, SO$_4^{2-}$, Cl$^-$, NH$_4^+$, and K$^+$. The fraction of sulfate, EC, and POC decreased as the pollution level increased, while those of SOC, NO$_3^-$, Cl$^-$, NH$_4^+$, and K$^+$ fraction increased and were most likely to be the driving factors. Five source factors were apportioned from the PMF model, and their importance decreased in the following order: secondary aerosol (32.30%) > traffic emission (23.90%) > biomass burning (23.30%) > mineral dust (14.4%) > coal combustion (6.2%). The PM$_{2.5}$ in Harbin was mainly affected by regional transportation from the
Harbin-Changchun megalopolis and slightly affected by long-distance transmission. Biomass burning and secondary aerosols were slightly affected by regional transportation, while traffic emissions, coal combustion, and mineral dust were severely affected. Traffic emissions were densely distributed in the Harbin-Changchun megalopolis, while coal combustion and mineral dust were scattered in wider regions, which was consistent with their distribution features.

This study mainly focused on episodes of pollution. The SPE in autumn was the most striking part period studied, and was characterized by longer-lasting and higher pollutant concentrations than those observed in the other periods. Among all chemical species, the concentrations of chlorine, potassium, carbonaceous components, SNA, SO₄, and N OR were particularly elevated, and SPE was most likely attributed to extensive biomass burning and enhanced secondary transformation, which contributed to 41.40% and 37.8% of the PM₂.₅, respectively.

The PEs were characterized by slightly elevated chemical species, and two categories were identified according to the different chemical features observed in the different episodes: pure-haze (PE1-PE3) in winter with a high proportion of secondary aerosol, and mixed haze-dust (PE4-PE7) with a high proportion of mineral dust. Enhanced heterogeneous reactions and weakened photochemical reactions were generally observed during pure haze events, which can be attributed to the high RH (>60%), low WS (3 m/s), suppressed PBL height (<200 m), and strengthened inversion layer under the control of the high-pressure system. In the mixed haze-dust event that occurred in spring, biomass burning activities, mineral dust, favorable diffusion, and regional transportation were observed, which may have caused the pollution episodes. In summary, the PEs were jointly caused by secondary aerosols (38.20%), traffic emissions (23.90%), coal combustion (16.10%), and mineral dust (14.40%).

Author contributions

Xiazhong Sun: Data curation, Formal analysis, Writing-Original draft preparation, Writing-Reviewing and Editing. Kun Wang: Resources, Methodology, Conceptualization. Bo Li: Resources. Zheng Zong and Xiaofei Shi: Methodology and Formal analysis. Lixin Ma, Donglei Fu and Samit Thapa: Investigation. Kersten, M., Smedes, F., 2002. Normalization procedures for sediment contaminants distribution features.

Declaration of competing interest

The authors declare that they have no conflict of interest.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cjclepro.2020.120275.

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