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Chemical characterization and synergetic source apportionment of $PM_{2.5}$ at multiple sites in the Beijing-Tianjin-Hebei region, China

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ABSTRACT: High frequencies of haze in China, especially in the Beijing-Tianjin-Hebei region, have received widespread attention in recent years. In this study, samples of filtered atmospheric fine particulate matter ($PM_{2.5}$) were collected synchronously at three urban sites (Beijing, Tianjin, and Shijiazhuang) and at a regional background site (Xinglong) for one month during each season from June 2014 to April 2015. Chemical composition determination/analysis, chemical mass closure, positive matrix factorization (PMF) and backward trajectory clustering were employed to investigate the chemical speciation, haze formation mechanism, emission sources, and influences of regional transport in North China. Our results reported that the aerosol chemical compositions were very similar at the urban sites and the background site and mainly comprised organic matter (16.0%-25.0%), sulfate (14.4%-20.5%), nitrate (15.1%-19.5%), ammonium (11.6%-13.1%) and mineral dust (14.7%-20.8%). Sources apportionment of $PM_{2.5}$ by PMF model revealed that secondary aerosols (background) and secondary inorganic aerosols (urban) were the dominant sources, which accounted for 29.2%-45.1% of $PM_{2.5}$ throughout the entire study and played a vital role in the formation and development of haze pollution. Emissions of motor vehicle exhaust exerted a significant impact on haze formation at urban sites, particularly at Beijing; and coal combustion also played an dominant role in winter, especially at Shijiazhuang. Backward trajectory analysis revealed that haze pollution has remarkable regional characteristics and usually occurs when air masses originated from polluted industrial regions of the south prevailed, which accompanied by high $PM_{2.5}$ loadings with high contributions of secondary aerosols. This study suggests that the control strategies to mitigate the haze formation in BTH region should be focused on the emission reduction of gaseous precursors from fossil fuel combustion, particularly from motor vehicles by improving the quality of oil products.

1 Introduction

Due to rapid economic development, rapid urbanization processes and excessive energy

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consumption, regional haze pollution has been recognized as the most severe environmental problem in China and has received the extensive attention of the government, public and scientists in recent years (Zhang et al., 2015b). Haze pollution mainly occurs in economically developed urban agglomeration; the most seriously polluted regions are typically the Beijing-Tianjin-Hebei (BTH) region, the Yangtze River Delta (YRD) region, the Pearl River Delta region (PRD) and the Sichuan Basin (Zhang et al., 2012; Zhang and Cao, 2015). The BTH region, which includes the two megacities of Beijing and Tianjin as well as Hebei Province, has the highest density of coal consumption and heavily polluting industries in China and is surrounded by Shandong, Henan, Shanxi and Inner Mongolia, which are all heavily populated, industrialized, urbanized and frequently reported to have serious haze pollution due to their intensive emissions of air pollutants across China (Liang et al., 2016; Wang et al., 2014a). Therefore, because the BTH region features the strongest pollutant emissions (Zhao et al., 2012) , unfavorable meteorological conditions (Cai et al., 2017; Xu et al., 2011), and its unique topography, extreme haze pollution, characterized by high particulate matter (PM) loading and very low visibility, has frequently occurred in this region. From 2014-2015, among the 190 priority pollution monitoring cities in China, the annual average concentration of atmospheric fine particulate matter ($PM_{2.5}$) was highest in the BTH region (Zhang and Cao, 2015). Additionally, this region is characterized by frequent dust storms and corresponding high mineral dust load episodes, especially in spring (Huang et al., 2010; Sun et al., 2010).

In addition to its the impacts on ecosystems, regional-scale atmospheric visibility, traffic safety, the economy, and interactions with climate (Zhang et al., 2015b), more importantly, such serious air pollution can have adverse effects on human health, including the increased risk of respiratory, cardiac and other medical conditions (Elliot et al., 2016; Wu et al., 2017), thus leading to increased mortality, especially in megacities, which are generally seriously polluted and densely populated. The health effects of PM are closely related to its chemical composition, in addition to the particle mass concentration and particle size (Zhang et al., 2015b). Tang et al. (2017) investigated the relationship between mortality and air pollution in Beijing from 1949 to 2011 and determined that the mortality in Beijing due to circulatory diseases was correlated with sulfate, nitrate and formaldehyde, whereas respiratory diseases were correlated with calcium, sulfate and nitrate, and malignant tumors were correlated with ammonium, nitrate and formaldehyde with an 11-year lag. In addition to their health impacts, the climate and environmental domino effects caused by PM are also closely related to the chemical compositions of PM, as have been widely reported (Tao et al., 2014; Wang et al., 2015b; Wu et al., 2009). These chemical constituents mainly originate from various anthropogenic sources, such as coal combustion, vehicle exhaust emissions, biomass burning, cooking, and industry-related emission, among others. Therefore, the key to reducing $PM_{2.5}$ concentrations and improving air quality is to control these sources; this necessitates a strong demand for good knowledge about the detailed chemical compositions of

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$PM_{2.5}$ in the BTH region.

Haze pollution has significantly regional characteristics. In addition to local emissions, the regional or inter-regional transport of primary PM and gaseous precursors plays an important role during haze periods (Chen et al., 2017; Li et al., 2017, 2015; Tao et al., 2012; Wang et al., 2014a; Ying et al., 2014). For example, the SO_2 measured in Beijing includes a large regional contribution transported from southern industrial areas (Guo et al., 2014). Therefore, these point to an urgent demand for wider collaborative work on emission control strategies with neighboring cities or provinces. For Shanghai, which is a megacity in the YRD region, Wu et al. (2017) estimated that the application of multiregional integrated control strategies in neighboring provinces could be most effective in reducing $PM_{2.5}$ in Shanghai and could largely reduce the economic loss caused by haze pollution. Haze pollution studies performed in the BTH region have obtained fruitful and meaningful results (Du et al., 2014; Liu et al., 2016a; Sun et al., 2013; Wang et al., 2014b; Zhang et al., 2014; Zhao et al., 2013c). The haze pollution in this region is primarily affected by low boundary layer height, southerly transport of water vapor and pollutants, and strong local emissions (Tang et al., 2015a; Zhu et al., 2016). Regional civil/industrial energy consumption and urban transportation are the main sources of atmospheric pollutants (Guo et al., 2014; Zhao et al., 2012). Compared to primary particles, secondary species that are transformed by gaseous precursors, including secondary inorganic aerosols (SIA) and secondary organic aerosols (SOA), play a more important role in the haze formation (Huang et al., 2014; Sun et al., 2012; Wang et al., 2013b; Zhang et al., 2014). Particularly under high relative humidity, aqueous chemistry process could be largely promoted and results in efficient secondary formation (Hu et al., 2016). Moreover, recent studies have reported that a new efficient formation mechanism of sulfate, that is the aqueous oxidation of SO_2 by NO_2 under the conditions of relative high humidity during haze events (Cheng et al., 2016; He et al., 2014; Wang et al., 2016a, 2013b). On the issue of haze mitigation strategies in Beijing, reducing regional emissions during the transition period and reducing local emissions during the polluted period was suggested (Tang et al., 2015a). However, because the studies describing the chemical composition and sources of $PM_{2.5}$ in the BTH region were often conducted at single site or for short periods, long-term and multisite studies are scarce (Li et al., 2017; Shen et al., 2016; Tian et al., 2016; Zhang et al., 2013; Zong et al., 2016). Single-site source apportionment data are not suitable for the comparing the results of different studies that used different methods of source analysis and data processing. Furthermore, studies of the source apportionment of $PM_{2.5}$ usually reflect the average condition for a given period, whereas the evolution of emission sources under different pollution levels has barely been investigated. Therefore, these studies yield a narrow view of their temporal and spatial characteristics and are not conducive to better understanding the mechanism of regional haze formation (Bressi et al., 2013).

To fill this gap, in this study, we conducted synchronous measurements of $PM_{2.5}$ at three

urban sites (Beijing, Tianjin, Shijiazhuang) in the BTH region and at one regional background site (Xinglong), analyzed their chemical compositions and quantified the apportionment of their sources using unified data processing and analytical methods. In addition, we emphatically analyzed the the chemical compositions and emission sources at different pollution levels and their differences between sites, as well as the influence of air masses originating from different directions. This study could provide an overall understanding of the regional signal of $PM_{2.5}$ pollution in the BTH region and support stakeholders and policy makers in understanding the impact of regional sources on the high loading of $PM_{2.5}$, thus facilitating the design of effective joint emission abatement strategies.

2. Materials and methods

2.1 Sites, sampling and meteorological data

Four sampling sites were selected in the Beijing-Tianjin-Hebei region (Fig. 1), including three urban sites (Beijing, Tianjin and Shijiazhuang) and a regional background site (Xinglong). These sites reflect the atmospheric pollutions condition in this region. The sampling site in Xinglong (117.58 °E, 40.39 °N) was located at Xinglong Observatory, National Astronomical Observatory, Chinese Academy of Sciences. Xinglong Observatory is located in the northeastern region of Beijing, which is located at a liner distance of approximately 110 km from Beijing and is surrounded by mountains and thus minimally affected by human activities. Therefore, it is one of the regional atmospheric background stations of the Chinese Academy of Sciences. The Beijing site (39.97 °N, 116.38 °E) was situated in the courtyard of the Institute of Atmospheric Physics (IAP), Chinese Academy of Sciences (CAS). The Tianjin site (39.09 °E, 117.19 °N) was located in the Tianjin Atmospheric Boundary Layer Observatory, Chinese Meteorological Administration, and the Shijiazhuang site (38.03 °N, 114.53 °E) was located in the Hebei Meteorological Service.

Meteorological data including ambient temperature, relative humidity and wind speed in Beijing were measured approximately 20 m to the filter sampling site, using an automatic meteorological observation instrument (Milos520, Vaisala, Finland), located at the 8 m measurement height. And in Tianjin, Shijiazhuang and Xinglong, the meteorological data was obtained from China Meteorological Administration.

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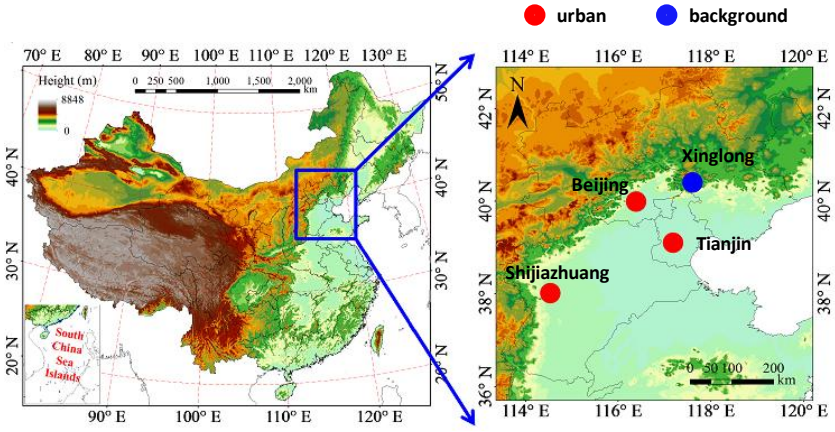

Figure 1. Map of the sampling sites (Beijing, Tianjin and Shijiazhuang are representatives of urban stations, whereas Xinglong represents the regional background)

$PM_{2.5}$ (particles with aerodynamic diameters of less than 2.5 μm) samples were synchronously collected at the four sites using a $PM_{2.5}$ sampler (TH-150C, Tianhong, Wuhan) from June 2014 to April 2015. During each season, we collected $PM_{2.5}$ samples on quartz membrane filters every day and night for one month, except on rainy days. The specific sampling period for summer extended from 15 June 2014 to 14 July 2014, that of autumn extended from 15 September 2014 to 14 October 2014, that of winter extended from 29 December 2014 to 27 January 2015, and that of spring extended from 20 March 2015 to 18 April 2015. The sampling time of each sample was 11.5 h, which generally occurred from 8:00 am to 19:30 pm during the daytime and from 20:00 pm to 7:30 am of the next day during the nighttime. During the entire observation period, a total sample number of 224, 214, 221 and 211 was collected at Beijing, Tianjin, Shijiazhuang and Xinglong, respectively.

Detailed records of the instrumental conditions were preserved during sampling, including the sampling time, the sampled-air volume, atmospheric pressure, air temperature, etc. After sampling, the quartz filters were individually placed in petri dishes and immediately stored at −20 ℃ prior to weighing and subsequent analysis. To ensure that the instrument worked at the specified flow rate, the airflow rate of the sampler was calibrated before and after each sampling. The carbon brush was replaced every month, and the outlet of the tail pipe was kept far away from the sampler in order to avoid contaminating filter samples. During the sampling process, strict quality control was conducted to avoid any pollution. The frequent cleaning of the cutter and tray of the membrane was basic and necessary.

2.2 Chemical analysis

2.2.1 Gravimetry

The quartz fiber filters, which were packaged with aluminum foil, were prefired in a muffle

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furnace at 500℃ for 4 h to remove organic materials. In addition, in order to minimize the influence of water adsorption, the filters were weighed before and after sampling using a microelectronic balance with a reading precision of 10 μg after undergoing a 48 h equilibration period inside a chamber under conditions of constant temperature (20±1 ℃) and humidity (45±5%). Atmospheric $PM_{2.5}$ masses were deduced from the gravimetric measurements performed before and after sampling. To guarantee the accuracy of the weighing, weighing was repeated until a difference between two measured weights of below 0.10 mg was achieved. All procedures were strictly quality-controlled to avoid any possible contamination of the samples.

2.2.2 Chemical analysis

A quarter of each sample was ultrasonically extracted with using 50 mL deionized water (with a specific resistivity of 18.2 MΩ/cm) for 30 min. After passing through microporous membranes with a pore size of 0.22 μm, the extracted solutions were analyzed using an ion chromatograph (IC) system (Dionex ICS-90, USA) for the detection of SO_4^{2-}, NO_3^-, NH_4^+, Cl^-, K^+, Na^+, Ca^{2+} and Mg^{2+}. More details are given by Huang et al. (2016).

A 0.495 cm^2 punch split from another quarter of each sample was used for the analysis of organic carbon (OC) and elemental carbon (EC), which was performed using a thermal/optical carbon aerosol analyzer (DRI Model 2001A, Desert Research Institute, USA) following the protocol of IMPROVE_A (TOR). Detailed procedures can be found in Cao et al. (2005) and Li et al. (2012).

The microwave acid digestion method was used to digest filter samples into liquid solution for elemental analysis. One quarter of each filter sample was placed in the digestion vessel with a mixture of 6 mL HNO_3, 2 mL H_2O_2 and 0.6 mL HF, and then was exposed to a three-stage microwave digestion procedure by a microwave-accelerated reaction system (MARS, CEM Corporation, USA). After that, the digestion solution was transferred to PET bottles and diluted to 50 mL with deionized water (with a conductivity of 18.2 MΩ/cm). Agilent 7500a inductively coupled plasma mass spectrometry (ICP-MS, Agilent Technologies, Tokyo, Japan) was used to determine the concentrations of 18 trace elements (TEs) in the digestion solution, including Mg, Al, K, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Ag, Cd, Tl and Pb). More detailed information, such as instrument optimization, calibration and quality control, is given by Wang et al. (2016b).

2.3 Data analysis method

2.3.1 Chemical mass closure

The chemically reconstructed $PM_{2.5}$ mass (PM_{chem}) was calculated to comprise eight categories of chemical species, which can be expressed as follows:

$$[PM_{chem}] = [\text{Organic matter}] + [\text{EC}] + [\text{Mineral dust}] + [\text{Trace metals}] + [\text{Sulfate}] + [\text{Nitrate}] + [\text{Ammonium}] + [\text{Chloride}]. \quad (1)$$

In estimating organic matter (OM), an OC to OM conversion factor of 1.6 was adopted for

aerosols at urban sites (Cao et al., 2007; Turpin and Lim, 2001) and the regional background site. Although the literature suggests that a higher OC to OM conversion factor of 2.1 is suitable for rural sites (Bressi et al., 2013; Turpin and Lim, 2001), we still used a uniform value of 1.6 for the sake of spatial comparisons. Therefore,

$$[OM] = 1.6 \times [OC]. \quad (2)$$

The calculation of mineral dust was performed on the basis of crustal element oxides (such as Al_2O_3, SiO_2, CaO, Fe_2O_3, TiO_2, MnO_2 and K_2O). The content of Ti is very low in atmospheric particulate matter and was usually 0.04 μg/m^3 in the atmospheric particles in Beijing, Tianjin and Shijiazhuang (Zhao et al., 2013c). Thus, eliminating the Ti content has an almost negligible influence on the estimation of the mineral dust. Mineral dust was calculated as:

$$[\text{Mineral dust}] = [Al_2O_3] + [SiO_2] + [CaO] + [MnO_2] + [Fe_2O_3] + [K_2O] = 2.14 \times [Si] + 1.89 \times [Al] + 1.4 \times [Ca] + 1.58 \times [Mn] + 1.43 \times [Fe] + 1.21 \times [K] \quad (3)$$

In this study, the measurement of trace elements in particles did not include the determination of Si, so the content of Si was calculated based on its ratio to Al in crustal materials, namely, [Si]= 3.41×[Al]. The calculations of K_2O and Fe_2O_3 were also based on their ratios to Al in crustal materials, considering that they have abundant artificial sources in addition to natural sources.

The trace metal content reflects the sum of 11 different heavy metal species and was expressed as:

$$[\text{Trace metals}] = V + Co + Ni + Cu + Pb + Zn + As + Se + Ag + Cd + Tl \quad (4)$$

The above chemical reconstruction method was applied to the four sites, and the comparison of the reconstructed results (PM_{chem}) with the membrane-weighing results (PM_{grav}) is shown in Figure S1. It can be clearly seen that PM_{chem} is significantly related to PM_{grav}, indicating that the chemical reconstruction method exhibited strong reliability. However, PM_{chem} concentrations at the four sites were all less than those of PM_{grav}, that is to say, there exsist unresolved matter that may largely be retaining water in the sampling membrane and particulate matter. Moreover, during the period between weighing and chemical measurement, the volatilization of organic matter and the decomposition of ammonium nitrate may occur. The discrepancy between PM_{chem} and PM_{grav} was thus defined as unknown.

2.3.2 PMF model

The EPA Positive Matrix Factorization (PMF) 5.0 model was applied to apportion the sources of $PM_{2.5}$ in this study, as it is an effective source apportionment receptor model that has been successfully applied to source apportionment in many cities and regions throughout the entire world (Huang et al., 2014; Reff et al., 2007). Compared to the CMB model (Chemical Mass Balance), the PMF model does not require source profiles prior to analysis, but only requires the values of the concentrations of sample species and their uncertainties (U.S. Environmental Protection Agency, 2014; Zhang et al., 2015c). In this study, model simulations were applied to

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datasets composed of 34 species: eight carbon fractions (OC1, OC2, OC3, OC4, OPC, EC1, EC2 and EC3), 8 inorganic species (SO_4^{2-}, NO_3^-, NH_4^+, K^+, Na^+, Ca^{2+}, Mg^{2+} and Cl^-), and 18 inorganic elements (Mg, Al, K, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Ag, Cd, Tl and Pb). Due to the low OC and EC concentrations at the background site, the entire concentration of OC and EC was input into the PMF model instead of the eight carbon fractions. In addition to the concentrations of the sample chemical species, the uncertainties of the sample species were calculated based on two different situations according to the PMF 5.0 user guide (U.S. Environmental Protection Agency, 2014):

If the concentration is less than or equal to the provided method detection limit (MDL) provided, the uncertainty is calculated using a fixed fraction of the MDL, as $Uncertainty = \frac{5}{6} MDL$.

If the concentration is greater than the provided MDL, the calculation is defined as $Uncertainty = \sqrt{(Error\ Fraction + Concentrtion)^2 + (0.05MDL)^2}$. In this study, the error fractions of SO_4^{2-}, NO_3^- and NH_4^+ were estimated at 5%, those of OPC, EC2 and EC3 were 15%, and those of other species were 10%.

3. Results and discussion

3.1 General characteristics of $PM_{2.5}$

3.1.1 Annual mass concentrations

Figure 2 reports the temporal variability of the gravimetrically determined $PM_{2.5}$ concentrations at the four sites (Beijing, Tianjin, Shijiazhuang and Xinglong) throughout the entire observation period. The strong day-to-day variability of $PM_{2.5}$ concentrations can be easily observed, especially in winter, when $PM_{2.5}$ ranging from 50.7 to 556.0 μg/m^3 at Shijiazhuang. These concentrations typically record periodic 'clean-polluted-clean' cycles for a few days, which were also reported by Guo et al. (2014), who noted that Beijing haze pollution underwent clear periodic cycles of 4–7 days in length. In addition to variations in source emissions and atmospheric processes, these periodic cycles of haze episodes are primarily driven by fluctuations in meteorological conditions (Guo et al., 2014; Zhang et al., 2015b), such as wind speed, relative humidity, air temperature/pressure, atmospheric stability, the height of the planetary boundary layer and air mass origins. Very similar patterns of $PM_{2.5}$ temporal variations were found at all four sites (Fig. 2), suggesting the homogeneous characteristics of atmospheric particulate matter on a regional scale. On average, the $PM_{2.5}$ annual concentrations throughout the entire observation period recorded higher levels at urban sites, which were 99.5, 105.7, 155.2 μg/m^3 at Beijing, Tianjin and Shijiazhuang, respectively, and represented values that were 1.5, 1.6 and 2.4 times those at the background site (Xinglong), respectively. This was particularly serious at Shijiazhuang, which consumes huge amounts of energy for industrial processes and daily life (Zhao et al.,

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2013b); during the entire observation period, 81% of samples at Shijiazhuang exceeded the second grade of the $PM_{2.5}$ daily average mass concentration in China (75 μg/m^3), followed by Tianjin (63%) and Beijing (55%) . In contrast, at Xinglong, only 29% of the total samples exceeded 75 μg/m^3, which may have mainly resulted from regional transport of pollutants from polluted areas.

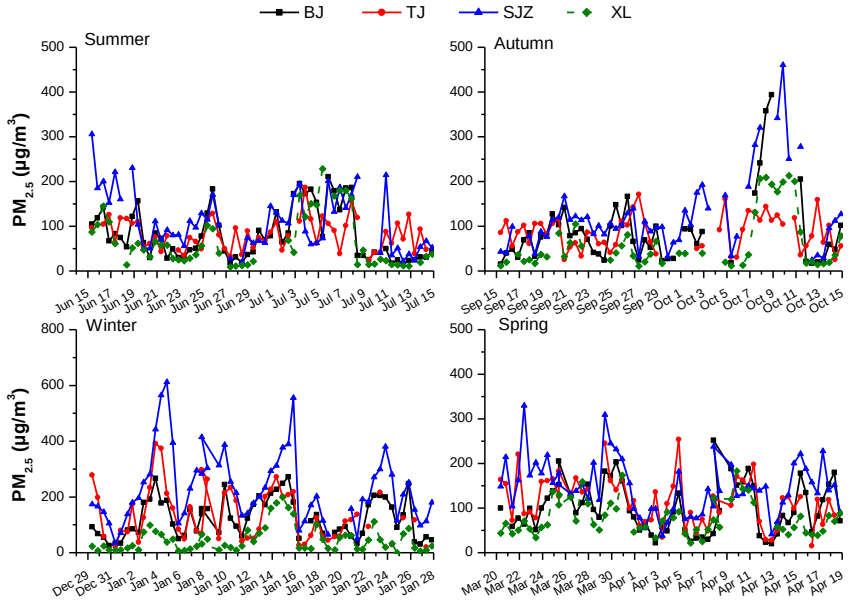

Figure 2. Time-series of gravimetric $PM_{2.5}$ concentrations during the four study periods

3.1.2 Seasonality

Due to the minor effects of anthropogenic emissions, the seasonal variations of $PM_{2.5}$ concentration at Xinglong were not significant (56.7-77.9 μg/m^3), and only slightly higher values were observed in spring. Zhao et al. (2009) also determined that maximum $PM_{2.5}$ concentrations usually occur during spring in Shangdianzi, which is another regional background area in the North China Plain. However, at urban sites, significant seasonal variations were observed, especially at Shijiazhuang. The highest $PM_{2.5}$ values were recorded in winter, with average concentrations of 124.8, 136.6 and 231.8 μg/m^3 at Beijing, Tianjin and Shijiazhuang, respectively. A large number of studies have also revealed that the heaviest haze pollution, with extremely high $PM_{2.5}$ loading, occurs in winter in the BTH region (Wang et al., 2012a; Zhang and Cao, 2015), which has mainly been attributed to the combination of intensive coal-fired heating and unfavorable meteorological conditions (i.e., more frequent occurrences of stagnant weather, temperature inversion and low boundary layer height) in this region (Tang et al., 2016a; Zhang and Cao, 2015; Zhao et al., 2009). Following winter, the average $PM_{2.5}$ concentrations in spring also remained at a relative high level at urban sites (101.0-148.4 μg/m^3), which may have partly

resulted from the enhanced mineral dust (see Fig. 5) produced by relatively high wind speeds during this season (Table S1). Due to strong turbulence occurring under conditions of strong radiation intensity and high temperature in summer, as well as the high atmospheric mixing layer generally observed in this season (Tang et al., 2016a), air pollutants could have been effectively diluted and diffused to some extent and thus resulted in the lowest measured $PM_{2.5}$ concentration during this season. In all four seasons, the $PM_{2.5}$ concentrations at Shijiazhuang were significantly higher than those at Beijing and Tianjin. In addition to intensity of the source emissions, meteorological parameters played an important role in this difference between sites, as Shijiazhuang recorded relatively high relative humidity and low wind speeds, which were both beneficial to the accumulation of $PM_{2.5}$ mass (Liu et al., 2017). Furthermore, the largest difference in the $PM_{2.5}$ average mass concentrations between urban sites and the background site occurred in winter, yielding values of 2.2-4.1 times those at Xinglong. This spatial difference could be explained by the strong intensity of pollution emissions in winter at urban sites.

3.2 Chemical components

3.2.1 Annual compositions

The chemical compositions of the entire sample set collected from the three urban sites and the regional background site were also similar, thus again confirming the regional homogeneity of atmospheric $PM_{2.5}$. The compositions of $PM_{2.5}$ in this region (Fig. 3) were primarily composed of organic matter (OM=OC×1.6, 16.0%-25.0%), secondary inorganic aerosols (SIA, including sulfate, nitrate and ammonium, 43.6%-53.1%), mineral dust (14.7%-20.8%); and lower proportions of EC (2.8%-6.2%), chloride (1.9%-5.5%), and trace metals (0.4%-0.6%). The annual average concentrations of carbonaceous aerosols (OM plus EC) were 31.1, 27.0 and 44.2 $\mu g/m^3$ at Beijing, Tianjin and Shijiazhuang, respectively, thus constituting large fractions (25.5%-31.2%) of $PM_{2.5}$ in the urban atmosphere. It is worth noting that the EC accounted for 6.2%, 5.9% and 5.7% of the mass of $PM_{2.5}$ at Beijing, Tianjin and Shijiazhuang, respectively, which are higher than that measured at Xinglong (2.8%), reflecting the strong emissions from fossil fuel combustion in urban areas. At Xinglong, lower concentrations and lower fractions of organic matter and higher fractions of mineral dust and SIA compared to those of urban sites were discovered. The presence of lower contributions of organic matter but higher contributions of SIA at the background site is consistent with the results measured on Qimu Island (another regional background site in North China, which is located approximately 300 km southeast of the BTH region) from 3 January to 11 February 2014 (Zong et al., 2016). This was mainly attributed to the regional-scale emission characteristics of gaseous precursors in this region, in which there are more abundant SO_2, NO_x, NH_3 emissions than OC emissions (Zhao et al., 2012), and the general characteristics of the regional atmosphere are accurately reflected at the regional background site.

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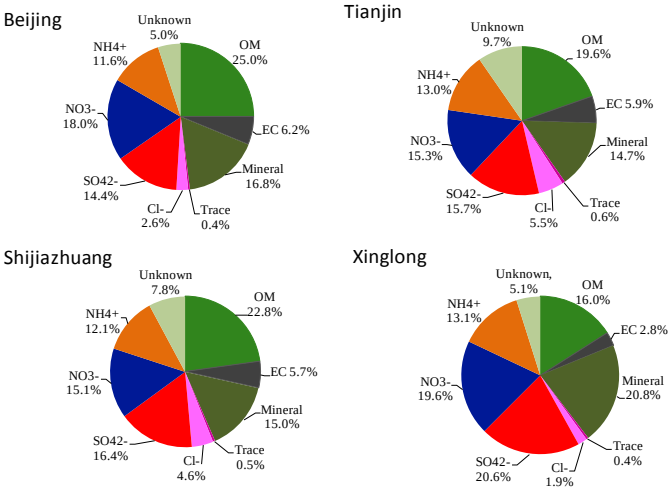

Figure 3. Pie charts depicting the relative contribution of major chemical components of gravimetric $PM_{2.5}$ based on annual data

As the key $PM_{2.5}$ constituents, sulfate, nitrate and ammonium, are generally recognized to originate from the secondary conversion of gaseous SO_2, NO_x and NH_3 through gas-phase chemical reactions and heterogeneous reactions (Wang et al., 2016a; Zhang et al., 2015b). In this study, they accounted for 14.4%-20.6%, 15.1%-19.6% and 11.6%-13.1% of the annual average gravimetric $PM_{2.5}$ concentrations, respectively. Among the three urban sites, the highest NO_3^- contribution (18.0%) was found at Beijing, which was in agreement with its strong traffic source. In addition, the mass ratio of NO_3^-/SO_4^{2-} at Beijing was 1.25, which was higher than that at Tianjin (0.97) and Shijiazhuang (0.92) as well as that at Xinglong (0.95). The NO_3^-/SO_4^{2-} mass ratio has often been used as an indicator of the relative contributions to aerosol particles from mobile versus stationary sources for sulfur and nitrogen in the atmosphere (Arimoto et al., 1996; Cao et al., 2009; Han et al., 2016), as vehicle exhausts and coal-combustion emissions are significant contributors to nitrate and sulfate, respectively (Huang et al., 2014). Therefore, the NO_3^-/SO_4^{2-} mass ratio was larger than 1.0 at Beijing, implying that the predominance of motor vehicle emissions over coal combustion in the contribution to PM pollution (Han et al., 2016), while at Tianjin and Shijiazhuang, coal combustion may still play a dominant role. However, compared to the reported results, the NO_3^-/SO_4^{2-} mass ratios at the two cities also increased from 0.85 (2009-2010) (Zhao et al., 2013b) to 0.92 (this study) at Shijiazhuang, as well as from 0.69 (2008) (Gu et al., 2011) to 0.75 (2009-2010) (Zhao et al., 2013b) and to 0.97 (this study) at Tianjin. This increasing trend also occurred in the background area, as the NO_3^-/SO_4^{2-} mass ratio at Xinglong increased from 0.78 (2009-2010) (Li, et al., 2013) to 0.95 (this study). These results clearly revealed that atmospheric nitrate pollution is worsening in this region, which is generally

recognized as being caused by increasing motor vehicle emissions and indicates the remarkable effect of the control measures of SO_2 emission.

In addition to carbonaceous and SIA aerosols, mineral dust was also a major component of these aerosols, which constituted a smaller fraction of the $PM_{2.5}$ concentrations (14.7%-16.8%) at urban sites than it did at the background site (20.8%). Cl^- exhibited higher concentrations and fractions at Shijiazhuang (7.2 μg/m^3, 4.6%) and Tianjin (5.8 μg/m^3, 5.5%) than it did at Beijing (2.6 μg/m^3, 2.6%) and Xinglong (1.2 μg/m^3, 1.9%), further illustrating the important contribution of coal combustion to $PM_{2.5}$ at Shijiazhuang and Tianjin. Trace element concentrations varied from 0.3 to 0.7 μg/m^3 and constituted only a minor fraction of $PM_{2.5}$.

3.2.2 Diurnal variation

The analysis of day-night variations indicates that the diurnal difference in the $PM_{2.5}$ annual average concentration was significant at urban sites, where values were 8%-19% higher in the nighttime than they were during the daytime, while negligible diurnal differences were found on the annual scale at Xinglong (Fig. 4). This obvious diurnal variation of $PM_{2.5}$ in urban areas was probably due to the apparent change in the height of the mixing layer between day and night (Zhao et al., 2009). Furthermore, strengthened burning activities may occur at night, as the night/day ratios of EC and Cl^-, which are both exclusively derived from primary emissions, were higher than those of $PM_{2.5}$. However, at Xinglong, the dominant source was from regional or long-range transport, with fewer contributions from local emissions; thus, the nocturnal stable boundary layer could have reduced the quantity of transmissions from the outside. Chemical compositions also recorded obvious diurnal variations, as the mass ratio of NO_3^-/SO_4^{2-}recorded higher values in the nighttime (0.99-1.39) than it did in the daytime (0.81-1.13), which is consistent with similar results obtained by Sun et al. (2016) conducted in Xianghe, which is located approximately 50 km southeast of Beijing. Such diurnal variation indicates the important role of gas-phase photochemical production of sulfate during the daytime, while the facilitated gas-to-particle partitioning of semi-volatile nitrate is associated with the low temperatures (Sun, et al., 2016) and effective hydrolysis of N_2O_5 at night, which is a major source of nitric acid in the urban atmosphere during the nighttime and can occur more efficiently on wet surfaces (Zhang et al., 2015b). In addition, the relatively static and stable meteorological conditions at night resulted in obviously lower fraction of mineral dust (11.3-17.0%, except for Tianjin), compared to those recorded during the daytime (18.3-24.3%).

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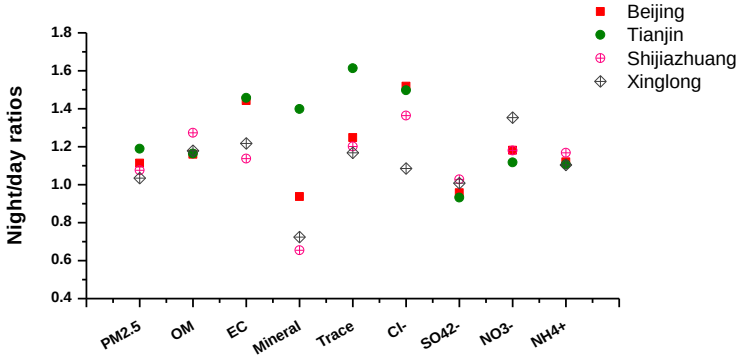

Figure 4. Day-night variations of $PM_{2.5}$ and its major compositions based on annual data

3.2.3 Seasonal variation of chemical components

The PM mass and its chemical compositions are governed by the chemical processes, evolution of emission sources and meteorological conditions (Bressi et al., 2013; Liu et al., 2017) , which usually exhibit seasonality. The seasonal pattern of $PM_{2.5}$ at urban sites was mainly driven by OM, SIA and mineral dust, which were the major components of $PM_{2.5}$ during each season. In winter, the dominant component at urban sites was OM; moreover, from Fig. 5, it can be seen clearly that the OM concentration and its contribution to $PM_{2.5}$ mass were significantly higher in winter (38.1-82.7 μg/m^3, 27.9-35.7%) than in other seasons. In addition, the EC concentration also reached a maximum value in winter at urban sites, yielding values of 11.8, 10.7 and 16.3 μg/m^3 at Beijing, Tianjin, and Shijiazhuang, respectively. Similar seasonal variations of carbonaceous aerosols were also observed in the BTH region (Beijing, Tianjin, Shijiazhuang, Chengde and Shangdianzi) (Zhao et al., 2013), Jinan (Yang et al., 2012) and the Pearl River Delta region (Cao et al., 2004). There are two possible explanations for this phenomenon. On the one hand, a substantial increase in the amount of coal-fires used for residential heating in winter could strengthen the abundance of carbon-containing emissions, including primary organic carbon, EC, and VOCs (Zhao et al., 2012). On the other hand, the lower temperatures in winter could favor the conversion from gaseous VOCs to their particulate form (Wang et al., 2015), whereas the high temperatures in warm seasons, especially in summer (during which the lowest OM concentrations can be seen in Fig. 5), may cause the semi-volatile organic compounds to mainly exist in their gaseous form in the atmosphere. Cl^-, which is a good tracer of coal combustion, also exhibited higher concentrations and contributions to $PM_{2.5}$ mass in winter (5.3-14.6 μg/m^3, 4.6-6.3%) than it did in other seasons (1.0-5.6 μg/m^3, 1.2-4.9%) at urban sites. However, since it is less affected by local anthropogenic sources, the Xinglong site recorded the lowest concentrations and contributions of EC and Cl^-, which showed no distinct seasonal variation.

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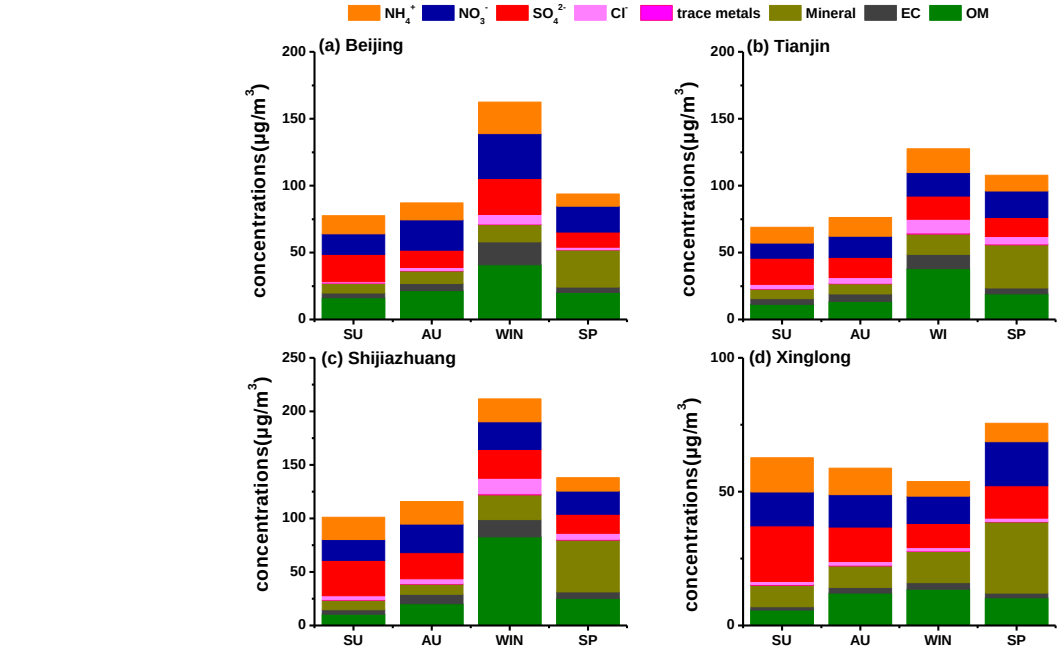

Figure 5. Seasonal variations of the major chemical components in the four sites (SU, AU, WIN, and SP represent the season of summer, autumn, winter and spring, respectively)

Unlike OM, SIA recorded the highest contributions in summer at urban sites (51.7-66.2%), which were significantly higher than those in winter and spring. The prominence of SIA in summer was more apparent at Xinglong (71.2%), which reflected the dominant contributions of meteorological factors. At urban sites, SIA also presented prominent contributions to $PM_{2.5}$ in autumn (51.9-58.1%) and the average $PM_{2.5}$ concentration was comparable in summer and autumn, which may have resulted from the high relative humidity in autumn, which is even higher than that in summer (Table S1). However, the contributions of sulfate and nitrate exhibited obvious seasonal differences at these three urban sites and even more apparent differences at the background site, recording greater contributions of sulfate in summer (23.6-29.9%) and nitrate in autumn (18.4-25.7%). This pattern was also found in our previous study in Beijing (Huang et al., 2016). This trend is closely related to their respective chemical/physical properties and mechanisms of generation, as nitrate tends to be decomposed under high temperatures (which mainly occurs in summer) due to the thermodynamic instability of ammonium nitrate, while the process of the chemical generation of ammonium sulfate (i.e., the gas-phase oxidation of SO_2 and subsequent heterogeneous reactions) is largely promoted under the high temperatures and intense solar radiation of summer (Huang et al., 2016; Ianniello et al., 2011; Zhang et al., 2015b).

In spring, the primary chemical component at all four sites was mineral dust, which contributed 27.5-34.1% to $PM_{2.5}$ and was significantly higher than it was in other seasons

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(7.5%-20.7%), thus reflecting the important influence of northwest dust on the atmospheric fine particles of the BTH region in spring and the increase of local resuspended dust (such as road dust and construction dust) resulting from the enhanced wind speed during this season (Table S1).

3.2.4 Chemical variations at different pollution levels

By using the $PM_{2.5}$ pollution grading standards of the Air Quality Index (AQI) technical regulations (HJ 633-2012) formulated by the Chinese Ministry of Environmental Protection as a reference, and considering the quantity of samples analyzed in this study, days with average concentrations of $PM_{2.5}<75$, $75 \leq PM_{2.5}<150$ and $PM_{2.5} \geq 150$ μg/m^3 were defined as clean, moderate pollution and heavy pollution days, respectively. The seasonal distribution of sample quantity at different pollution levels was listed in Table S2. Figure 6 shows the concentrations of chemical compositions and the percentage of the sample quantity at different pollution levels throughout the entire campaign at each site, from which we can see that aerosol pollution was most serious at Shijiazhuang with only 19% at clean level and 42% at heavy pollution level. With the deterioration of pollution, nearly all chemical components increased continuously and noticeably A remarkable increase of carbonaceous aerosols was observed during the pollution process, in which the average OC and EC concentration on heavy pollution days were 3.5-7.0 and 4.6-5.9 times as high as they were on clean days, respectively. At each pollution level, both OC and EC concentrations were lowest at Xinglong and highest at Shijiazhuang. The OC/EC mass ratio decreased significantly with pollution levels at Beijing, with its value varying from 3.4 (clean days) to 2.7 (moderate pollution days) to 2.1 (heavy pollution days). Tianjin also recorded a similar trend (varying from 2.3 to 2.4 to 1.7, respectively), but this change was less apparent than that at Beijing. As reported by Watson et al. (2001), lower OC/EC ratios are emitted from motor vehicles (1.1) than are emitted from coal combustion (2.7) and biomass burning (9.0). Saarikoski et al. (2008) have also documented OC/EC ratio of 6.6 for biomass burning and 0.71 for traffic emissions. Moreover, the OC/EC ratio for diesel vehicles has been observed much lower value than that for gasoline vehicles (Na et al., 2004). Therefore, we speculate that this pattern of variation of the OC/EC mass ratio at Beijing may be influenced by the strengthened contributions of local motor vehicle exhaust under heavily polluted conditions due to weakened regional transport, which usually contributes most during the initial and growth stages of haze episodes while decreasing during the peak pollution stage, this mechanism has been confirmed in some pollution processes in Beijing (Liu et al., 2016b; Tang et al., 2015a). Therefore, the fact that the OC/EC ratio increases with the increasing development of haze pollution indicates the key role of local traffic emission in the haze progress at Beijing. However, the OC/EC mass ratio increased on heavy pollution days (from 2.2 to 2.7) at Shijiazhuang, indicating that there are different haze formation mechanisms and pollution sources at Shijiazhuang. Different from the key role of local motor vehicle exhaust in the severe haze period at Beijing, at Shijiazhuang, the emissions of coal

combustion may dominate the haze pollution and accumulate constantly. In addition, the secondary formation of SOA from VOCs may be more significant during the pollution process at Shijiazhuang, as the fact that more remarkable increase of OM contribution to $PM_{2.5}$ was observed at this site.

In addition, SIA significantly contributed to the enhancement of $PM_{2.5}$ mass during pollution events, from 16.5-29.5 μg/m^3 on clean days to 46.7-77.6 μg/m^3 on moderate pollution days to 91.8-132.7 μg/m^3 on heavy pollution days. Many studies have shown that enhanced heterogeneous reactions under conditions of relatively high humidity are the main reason for the increased SIA during haze periods (Huang et al., 2016; Sun et al., 2013; Wang et al., 2012b). The growth of SIA was particularly important in the haze formation at Beijing and Xinglong, as the SIA contribution increased significantly, from 34.5% on clean days to 44.2% on moderate pollution days to 51.3% on heavy pollution days at Beijing, and from 41.2% to 57.5% to 68.3%, respectively, at Xinglong. At Beijing, among the three secondary inorganic components, only the contribution of nitrate recorded a pronounced increase during the pollution process, thus indicating that haze pollution in Beijing mainly resulted from the secondary transformation of NOx that was mainly derived from local traffic emissions, and once again reflecting the dominant contribution of local motor vehicle exhaust in haze episodes. In contrast to that observed at Beijing, sulfate, nitrate and ammonium all clearly increased with the deterioration of pollution at Xinglong, suggesting that its high $PM_{2.5}$ loadings mainly resulted from the intensifying secondary transformations of gaseous pollutants (SO_2, NO_x and NH_3) during stagnant meteorological conditions in the background area. An average increase in the contributions of SIA during the pollution process was not observed at Tianjin and Shijiazhuang, but did occur in all seasons except for spring. The mineral dust contribution increased on heavy pollution days in spring at Tianjin and Shijiazhuang, indicating the important role of soil dust in the formation of spring haze at the two study sites.

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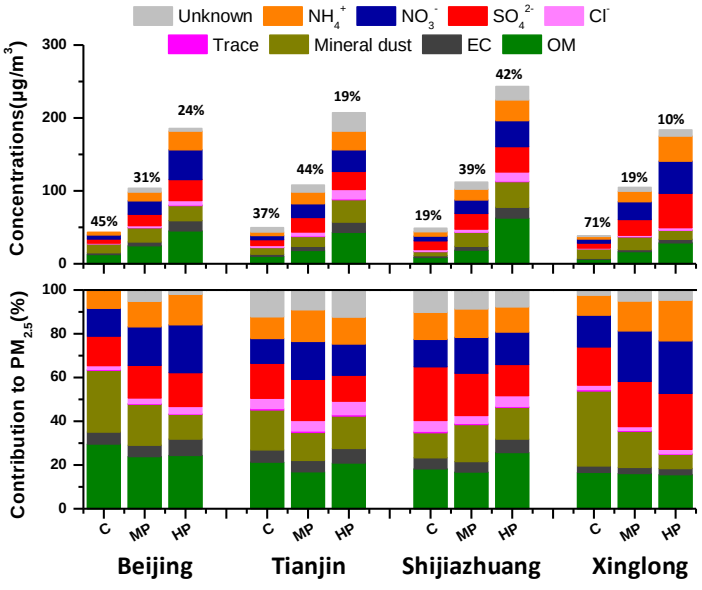

Figure 6. The evolution of chemical components at different pollution levels throughout the entire study period. C, MP, and HP represent clean days ($PM_{2.5}$＜75 μg/m^3), moderate pollution days (75≤$PM_{2.5}$＜150 μg/m^3) and heavy pollution days ($PM_{2.5}$≥150 μg/m^3), respectively. "%" represents the proportion of filter sample quantity at each pollution level in total samples.

3.3 Source apportionment by PMF

3.3.1 Identified sources

The sources/factors of $PM_{2.5}$ at three urban sites were apportioned by applying the receptor model PMF; this was also performed at Xinglong for comparison. The identification of the sources was based on certain chemical tracers which are generally presumed to be emitted from specific sources and present in significant amounts in the collected samples (Singh et al., 2016). Based on this, eight factors were identified for Beijing and Tianjin, whereas nine were identified for Shijiazhuang and only five were identified for Xinglong. The relative dominance of each source varied by site and season. Contributions of the identified sources determined by analyzing the annual data are shown in Fig. 8; the factor profiles of $PM_{2.5}$ for the regional background site (Xinglong) are listed in Fig. 7, while those for the urban sites are shown in Supplementary Fig. S2-4. These factors can be summarized as follows:

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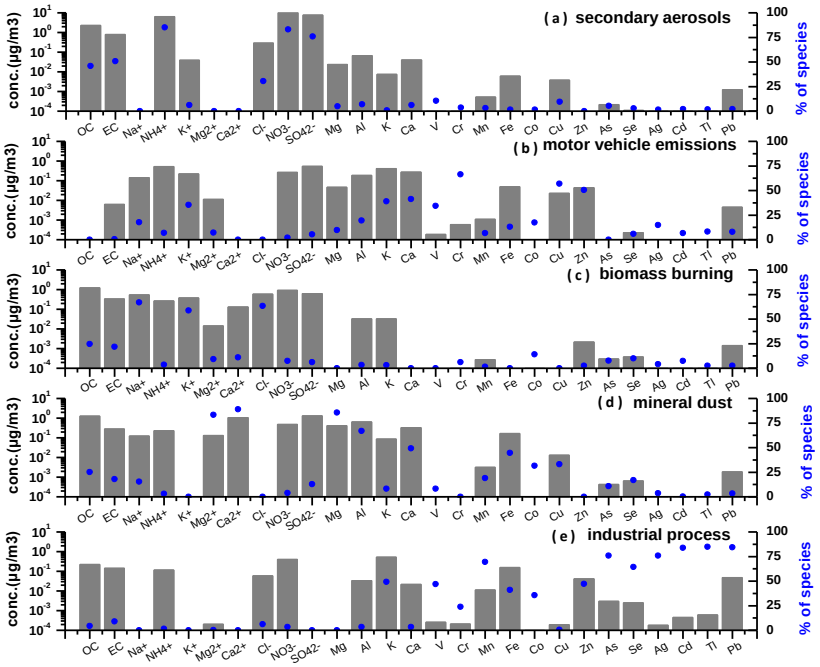

Figure 7. PMF factor/source profiles for $PM_{2.5}$ samples throughout the entire study period at Xinglong in concentration (μg/m^3) and percentage (%)

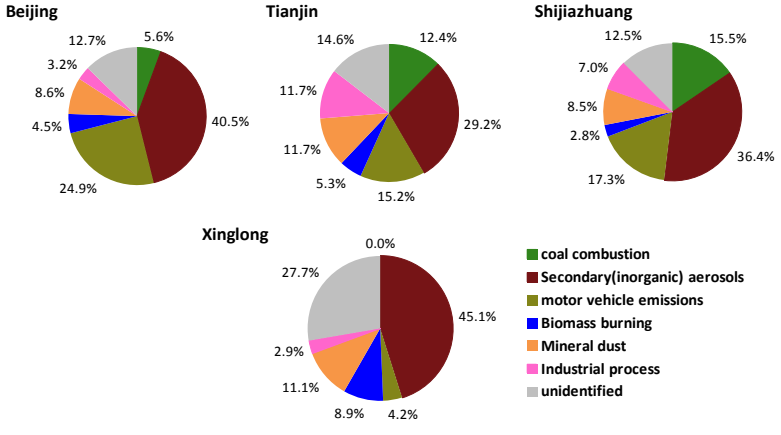

Figure 8. The annual contributions of identified sources to $PM_{2.5}$ mass at the four sites

(ⅰ) Coal combustion. In China, coal combustion is generally used in thermal power plants, as well as for winter residential heating in its northern cold regions. This source is characterized by high loadings of OC, EC, and chloride, most of which were apportioned in this factor (Fig. S2-4 a). At the three urban sites, the coal combustion source exhibited significantly higher

concentrations (17.6, 31.6 and 67.8 μg/m^3 at Beijing, Tianjin and Shijiazhuang, respectively) and contributions to $PM_{2.5}$ (14.1%, 23.3% and 29.2%, respectively) in winter, than were seen in other seasons (which recorded concentrations of 0.6-16.1 μg/m^3 and contributions of 0.7-10.7%). This was strongly aligned with the seasonal characteristics of coal combustion activity in this region. The annual average emissions from coal combustion contributed 5.6% to $PM_{2.5}$ at Beijing and were even higher at Tianjin (12.4%) and Shijiazhuang (15.6%), but were not identified at Xinglong.

(ii) Secondary aerosols/inorganic aerosols. The dominant source of the four studied sites was secondary inorganic aerosols at three urban sites (29.2%-40.5%) and secondary aerosols at Xinglong (45.1%). At Xinglong, this factor (Fig. 7a) could be identified as secondary aerosols because of its high contributions and accumulations of OC, sulfate, nitrate and ammonium, which caused it to include SIA and SOA. In addition, approximately 30% of total chloride was assigned to this source, indicating that a coal combustion source was included in the secondary aerosol source. However, our above analysis indicates that there were only very minor local coal combustion emissions at Xinglong. Therefore, this can probably be attributed to the regional transport of coal combustion emissions, along with secondary sources.

At Tianjin, high contributions of ammonium, nitrate and sulfate, which comprise most of their mass concentrations, were apportioned in the secondary aerosol factor (Fig. S3b) with only minor OC, thus, we identified this factor as the source of secondary inorganic aerosols. In contrast, at Beijing and Shijiazhuang, secondary inorganic aerosols were further separated into two sources defined as nitrate-rich secondary (Fig. S2b and S4b) and sulfate-rich secondary aerosols (Fig. S2c and S4c), which record the respective characteristics of prominent contributions of ammonium/nitrate and ammonium/sulfate. Consistent with the generating mechanism and seasonal characteristics of nitrate and sulfate, the contribution of nitrate-rich secondary aerosols to $PM_{2.5}$ had the highest values in autumn, whereas the sulfate-rich secondary aerosols had the highest contribution values in summer at Beijing and Shijiazhuang.

(iii) Motor vehicle emissions. Emissions from motor vehicles are crucial to serious air pollution, especially in economically developed megacities. In our study, the source of motor vehicle emissions, which have high concentrations of OC, EC, and the trace metals of Cu, Zn and Pb and are considered to be characteristic species of bake wear dust and tire wear dust (Karnae and John, 2011; Tian et al., 2016; Zhang et al., 2013), was identified at all four study sites, contributing 24.9% (Beijing), 15.2% (Tianjin) and 17.3% (Shijiazhuang) at the urban sites and only 4.2% at Xinglong. This suggested the important role of motor vehicle exhaust in the urban $PM_{2.5}$ pollution, especially in Beijing, where the quantity of motor vehicles increased to 5.7 million by 2016 (http://www.chinaidr.com/tradenews/2017-03/111537.html). Notably, secondary aerosols are mainly produced by the gas-to-particle transformation of SO_2, NO_X, NH_3, and VOCs, and motor vehicle exhaust is an important source of the emissions of NO_X and VOCs in urban

areas (Huang et al., 2011; Tang et al., 2016b). Therefore, the actual contributions of motor vehicle emissions to particles should be higher if considering the secondary formation of gaseous exhaust in the atmosphere. Since 2017, vehicular emission standard of China in Phase Ⅴ (equivalent to European Ⅴ) has been implemented on a national scale, and has caught up with the developed countries. However, less restrictive standard of oil quality in China than that in Europe and United States is the main reason for the strong motor vehicle emissions, particularly the limits standard of aromatics and alkenes. These two unsaturated hydrocarbon species have an important effect on air quality (Schell et al., 2001), as decreasing alkenes contents can decrease the fire temperature and reduce NOx emissions (Tang et al., 2015b). A new research also reported that gasoline aromatic hydrocarbons performed an essential role in urban SOA production enhancement and thus significantly affected on ambient $PM_{2.5}$ (Peng et al., 2017). The limits standards of aromatics and alkenes contents in vehicle gasoline are respectively 40% and 28% for China IV implemented since 2014, 40% and 24% for China Ⅴ since 2017, 35% and 18% for China Ⅵ suggested to be implemented in 2019 (http://www.nea.gov.cn/). In contrast, the limits standard of 35% for aromatics and 18% for alkenes (European IV) in Europe was implemented since 2005 (Tang et al., 2015b). In addition to lower standards, the phenomenon of substandard oil products also exists, as Tang et al. (2015b) reported that 48.4% of gasoline samples in North China exceeded the limit standard of aromatics (40%).

(ⅳ) Biomass burning. Biomass burning emissions in northern China are mainly produced by the burning of agricultural straw and thus often appear during the farming and harvest seasons and can have a significant impact on the atmospheric chemistry and climate on both a regional and global scale (Duan et al., 2004; Li et al., 2010; Sun et al., 2016). The source profiles of factors defined as biomass burning (Fig. 7c, Fig. S2e, S3d and S4e) were rich in K^+, which is widely regarded to be a good tracer of biomass burning sources. In addition to K^+, the fresh smoke plumes of burning biomass also contain a significant amount of Na^+, Cl^-, OC and EC (Wang et al., 2013a), which were also found in the profile of biomass burning in this study. The annual average contribution of biomass burning to $PM_{2.5}$ exhibited higher values at Xinglong (8.9%) than it did at the three urban sites (2.8%-5.3%). In addition to its high proportion during the harvest season (autumn, 11.6%), biomass burning emissions exhibited their highest contributions to $PM_{2.5}$ in winter at Xinglong (14.6%) and recorded low values (1.0%-4.4%) in winter at the three urban sites. This can likely be attributed to the fact that a single type of fuels is used by the surrounding residents, as bio-fuels (i.e., straw and dry wood) are always utilized for cooking and winter heating (Zhao et al., 2012), which is totally different than the matter used for energy (mainly coal and natural gas) by urban and suburban residents. Similar to the motor vehicle source, the contribution of biomass burning would be higher if considering its emissions of secondary aerosol precursors (VOCs, SO_2 and NOx), especially VOCs (Bo et al., 2008; Li et al., 2014; Yuan et al., 2010).

(ⅴ) Mineral dust. Road dust from local traffic and construction activities (with abundant

concentrations of Mg^{2+}, Ca^{2+} and motor vehicle-related species such as Cu, Zn and Pb) (Han et al., 2007) and soil dust, which is mainly derived from long-range transport (and is more enriched in Al, Ca, Fe, Mg and Mn) were summarized as mineral dust. This source was found to have obvious seasonality, exhibiting its highest contributions in spring at urban sites (17.2%-21.0%) and the background site (22.2%). Influenced by dust from the northwest, this seasonal variation was most significant and regular for soil dust. The factor of road dust was identified at the three urban sites, which contributed annual average values of 3.5%-7.8% to $PM_{2.5}$, but was not extracted from mineral dust at Xinglong due to the minor influence of anthropogenic sources.

(vi) Industrial process. A striking feature of this source was its relatively high concentrations of mining-related elements, such as V, Mn and Fe, and elements related to pollution produced by industrial processes, including As, Se, Ag, Cd, Tl and Pb. More than 50% of the mass concentrations of the above pollution elements were allocated in the source. The annual average emissions from industrial processes contributed 3.2%-11.7% to $PM_{2.5}$ at urban sites, which was lowest at Beijing. The industrial process source (2.9%) at Xinglong may have resulted from the regional transport from regional cities with heavy industrial activity. At Tianjin and Shijiazhuang (two heavily industrial cities), an oil refining/metal smelting source, characterized by high concentrations of V, Mn, Fe, Co and Ni (Mohiuddin et al., 2014), was extracted from the emission source of industrial processes, contributing 2.8% (Tianjin) and 0.7% (Shijiazhuang) to $PM_{2.5}$.

3.3.2 Clean days versus hazy days

During the transition from clean to pollution processes, significant variations in the contributions of sources/factors contribution were observed, which exhibited strong seasonal features and spatial heterogeneity (Fig. 9). However, the common characteristic in each season or site was that secondary aerosols/inorganic aerosols played a key role in the development of haze pollution, which generally recorded increasing contributions with worsening pollution (except in spring at Shijiazhuang), which was also reported by Huang et al. (2014). Especially in summer and autumn, the source of secondary inorganic aerosols increased most dramatically as a function of high relative humidity and suitable temperature at urban sites; on heavy pollution days, it accounted for 55.7%-75.2% of $PM_{2.5}$ in summer and 55.0%-61.5% in autumn, thus representing the biggest source of atmospheric $PM_{2.5}$ during these two seasons. In contrast, at Xinglong, the secondary aerosols source was always the dominant factor in haze formation, which accounted for 66.7%, 67.5%, 68.4% and 87.0% of $PM_{2.5}$ on heavy pollution days in summer, autumn, winter and spring, respectively. In addition, biomass burning was also another important source during the winter pollution process at Xinglong.

In contrast to background site, the emission sources and generation mechanism of haze pollution were more complex at urban sites, especially in winter, as primary emissions such as motor vehicle emissions, coal combustion and industrial processes were also the main sources of

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heavy pollution in winter. As the main fuel for winter heating in the North China Plain, the contribution of coal combustion to $PM_{2.5}$ mainly occurred in winter and was key to the heavy pollution in winter in urban areas, as it increased with increasing pollution levels. Especially at Tianjin and Shijiazhuang, it contributed nearly 30% to $PM_{2.5}$ on heavy pollution days and contributed even more if considering the secondary formation of sulfate from the SO_2 that was largely emitted by coal combustion. Moreover, the primary emissions of motor vehicles also exerted a remarkable impact on the winter haze pollution, accounting for 25.5% and 23.2% of $PM_{2.5}$ on heavy pollution days at Beijing and Shijiazhuang, respectively, and accounting for more if considering the secondary conversion of gaseous pollutants in the vehicle exhaust. Especially on hazy days, low visibility could aggravate urban traffic congestion during rush hour, thus causing more pollutants to be emitted by motor vehicles when operating in this condition (Zhang et al., 2011).

In spring, the effect of mineral dust was also highlighted at urban sites. Most notably, at Shijiazhuang, mineral dust significantly contributed to the aerosol pollution process, as its contribution to $PM_{2.5}$ continuously increased from 9.7% on clean days to 18.6% on moderate pollution days to 22.9% on heavy pollution days. However, along with the increase in pollution levels, the ratio of local road dust in mineral dust decreased from 81.6% (on clean days) to 50% (on pollution days), thus reflecting the significant impact of long-range transported northwest dust on the spring aerosol pollution at Shijiazhuang.

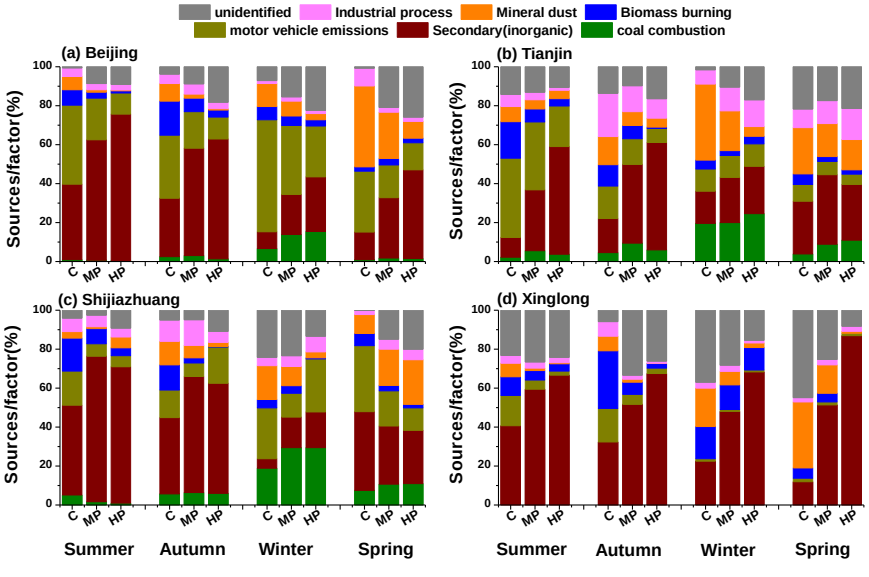

Figure 9. Fractional contribution of sources/factors to $PM_{2.5}$ mass at different pollution levels during each season at Beijing (a), Tianjin (b), Shijiazhuang (c) and Xinglong (d)

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3.4 Backward trajectory

A 48 h backward trajectory analysis with a 12 h interval using the hybrid single-particle Lagrangian integrated trajectory (HYSPLIT 4.9) model was conducted at all four sites. To reveal the pollution patterns and source signals of $PM_{2.5}$ carried by air masses from different directions and regions, the source contributions of $PM_{2.5}$ were grouped according to their trajectory clusters, as shown in Fig. 10. The results in Fig. 10 indicate the important effect of regional transport on the $PM_{2.5}$. More than half of the air masses (54%, 64%, 51% and 56% for Beijing, Tianjin, Shijiazhuang and Xinglong, respectively) throughout the entire study period were from the BTH region and Shandong Province. These air masses, which move with weak speeds and at low heights could have carried abundant atmospheric pollutants (i.e., particles and gaseous pollutants) from the areas through which they passed, which may have been accompanied by plenty of water vapor during transport (Tao et al., 2012; Zhu et al., 2016), resulting in high $PM_{2.5}$ mass concentrations driven by the local secondary formations at the sampling sites. The air masses (cluster 1 at each site) from the southern direction caused the most serious pollution. Air masses originating from Mongolia were also dominant (27%-46%) in this region (cluster 2-3 at Beijing, cluster 4-5 at Tianjin, cluster 3-4 at Shijiazhuang and cluster 3 at Xinglong), especially in winter, and $PM_{2.5}$ in these clusters were generally lower than those from the surrounding polluted areas, except for Shijiazhuang and Tianjin in cluster 5 (Fig. 10b). In addition, a small proportion of air masses originating from the Hulunbuir prairie in Inner Mongolia, such as cluster 3 at Tianjin and cluster 4 at Xinglong, could have carried clean air to the sampling sites, thus causing the corresponding $PM_{2.5}$ mass concentrations to be the lowest. In contrast to other sites, high average $PM_{2.5}$ concentrations in each cluster were observed at Shijiazhuang, especially in cluster 2, which originated from Inner Mongolia and passed over Shanxi Province before arriving at the sampling sites, and corresponded to be highest $PM_{2.5}$ value (178.9 $\mu g/m^3$). Although cluster 4 originated from Mongolia and traveled with fast speed and great height, the $PM_{2.5}$ was indeed higher than that of cluster 1, which may be because it passed over Inner Mongolia and Shanxi Province and thus could have carried many pollutants from these polluted areas. The $PM_{2.5}$ concentration in cluster 3, which originated from Mongolia and passed over Inner Mongolia and northern Hebei (a relatively clean area in the BTH region), was relatively lower (102.1 $\mu g/m^3$). However, the heavy pollution at Shijiazhuang was mainly dominated by cluster 1 (51%) from the south, as cluster 2 and cluster 4 accounted for only 23% and 13% of the trajectories, respectively. Similarly, haze pollution at Beijing, Tianjin and Xinglong also developed due to the presence of weak southerly air masses from heavily polluted regions. This is consistent with the results of Guo et al. (2014) and Li et al. (2015).

In addition to the different $PM_{2.5}$ concentrations in different clusters, large differences in the source contributions were also found. For example, at Shijiazhuang, high $PM_{2.5}$ concentrations was observed in each cluster. However, it could also be clearly seen that the source contribution

charts of these clusters were very different, and that the air masses originating from the BTH region and Shandong Province were characterized by high contributions of secondary inorganic aerosols, while air masses from long-range transport were more enriched in mineral dust. Therefore, at Shijiazhuang, the contributions of secondary inorganic aerosols was occurred in the sequence of cluster 1> cluster 2> cluster 3> cluster 4, whereas those of mineral dust exhibited the opposite pattern. Similar patterns were also observed at Xinglong, Beijing and Tianjin in this study. This pattern of secondary inorganic aerosols was also observed by Zhang et al. (2014) in their study in Beijing. As mentioned in Section 3.1, secondary aerosols were primarily attributed to the transformations of their precursors (SO_2, NOx, NH_3 and VOCs). The slow and near-ground air masses originating from regional polluted areas could have resulted in stagnant conditions, which could have been conducive to the accumulation of precursors from local emissions and transported in, and to the following secondary transformation. Furthermore, during this transportation, the carried gaseous pollutants also could have undergone secondary transformations and directly resulted in a rapid increase in $PM_{2.5}$ concentrations in the downwind area (Bressi et al., 2014; Li et al., 2015). Our previous study also have revealed that the high concentrations of organic aerosols (OA) in Beijing, especially low-volatility oxygenated aerosols that are more oxidized and aged, were associated with southerly originated air masses containing secondary regional pollutants (Zhang et al., 2015a).

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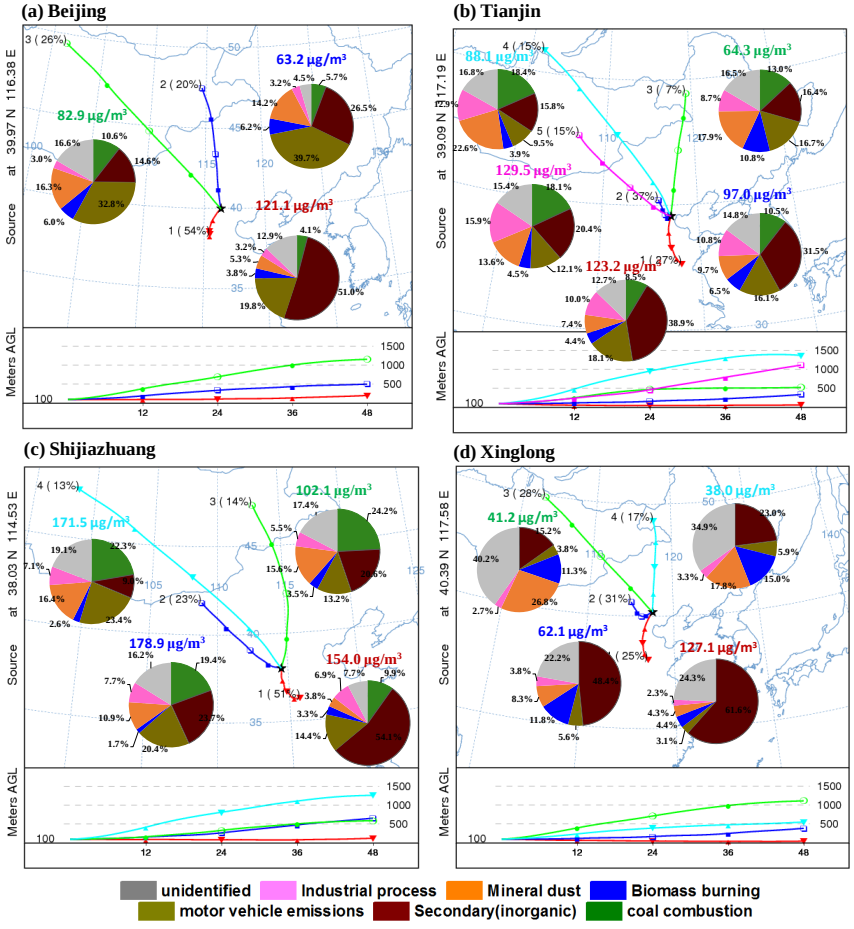

Figure 10. Source contributions resolved from PMF at each 48 h backward trajectory cluster during the entire study period at Beijing (a), Tianjin (b), Shijiazhuang (c) and Xinglong (d)

4. Conclusions

In this study, the chemical compositions and emission sources of fine particulate matter ($PM_{2.5}$) were comprehensively investigated in three urban sites (Beijing, Tianjin and Shijiazhuang) and a background site (Xinglong) at the Beijing-Tianjin-Hebei region. The temporal variations of $PM_{2.5}$ and its chemical components recorded homogeneous features at the four sites, reflecting the regional characteristics of aerosol pollution. However, obvious seasonal and spatial variability of $PM_{2.5}$ and its chemical compositions was observed. Severe $PM_{2.5}$ pollution was found at urban sites, especially at Shijiazhuang, and relatively clean at background site. The seasonal variation of $PM_{2.5}$ concentration at Xinglong was not significant due to the presence of fewer anthropogenic emissions; at urban sites, the lowest $PM_{2.5}$ value was observed in summer and the highest value was observed in winter, likely due to the prevalence of winter coal-fired heating and unfavorable

meteorological conditions. In terms of chemical compositions, the major chemical components in this region were organic matter (16.0%-25.0%), sulfate (14.4%-20.6%), nitrate (15.1%-19.6%), ammonium (11.6%-13.1%), mineral dust (14.7%-20.8%) and its minor components were EC (2.8%-6.2%), chloride (1.9%-5.5%), and trace metals (0.4%-0.6%). These chemical components exhibited their own seasonal and diurnal variation characteristics which were closely related to chemical processes, emission sources and meteorological conditions.

The PMF model-resolved source analysis showed that coal combustion, motor vehicle emissions, secondary inorganic aerosols, mineral dust and industrial processes were the main sources of $PM_{2.5}$ in urban areas; however, the dominant source at the background site was secondary aerosols. The drastic secondary formation of gas precursors was the dominant cause of aerosol pollution, especially in summer and autumn. In winter, coal combustion exerted an important impact on the haze formation in urban areas; in spring, mineral dust also exerted a significant impact. In urban atmospheres, especially in Beijing, the contribution of motor vehicle emissions was also prominent in haze formation, as it is the major source of gaseous NOx. However, in this study, we could not determine the exact contribution of the secondary transformation of NOx emitted by motor vehicles. Future studies should be further investigated of additional details about these secondary aerosols.

Haze pollution has remarkable regional characteristics, severe pollution in BTH region was mainly influenced by the region itself and surrounding polluted areas of the south. Therefore, we question the efficiency of the abatement strategies of the emission reduction and air quality improvement and request a joint collaboration of cities in this region, even throughout all of northern China. Emission reduction of gaseous precursors from fossil fuel combustion, especially from motor vehicles by improving oil quality, are essential to mitigate the severe haze pollution in BTH region.

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