A review of atmospheric fine particulate matters: chemical composition, source identification and their variations in Beijing

Yinjie Ma [a,b], Yuhan Huang [c,*], Jianghua Wu [a], Jiaqiang E [a,b,*], Bin Zhang [a], Dandan Han [a],

Hwai Chyuan Ong [d]

[a] College of Mechanical and Vehicle Engineering, Hunan University, Changsha 410082, China

[b] Institute of New Energy and Energy-Saving & Emission-Reduction Technology, Hunan University, Changsha 410082, China

[c] Centre for Green Technology, School of Civil and Environmental Engineering, University of Technology Sydney, NSW 2007, Australia

[d] Future Technology Research Center, National Yunlin University of Science and Technology, Yunlin 64002, Taiwan ROC

* Correspondence:

Professor Jiaqiang E, ejiaqiang@hnu.edu.cn; Dr Yuhan Huang, yuhan.huang@uts.edu.au

Abstract

Fine particulate matter ($PM_{2.5}$) is a major air pollutant worldwide. Characterizing its chemical compositions and source contributions is a critical prerequisite for effective control of $PM_{2.5}$ pollution. This paper systematically reviews the sampling methods, chemical compositions and source apportionments of $PM_{2.5}$. Sampling methods have significant influences on the identification of chemical compositions and source contributions, with Quartz and Teflon filters being the most widely used. Receptor models are commonly adopted for identifying the sources of $PM_{2.5}$, such as positive matrix factorization, chemical mass balance, principal component analysis and UNMIX models, which have their respective advantages and limitations that determine their applications. The variations of $PM_{2.5}$ compositions and sources in the past two decades in Beijing are also reviewed, which is the political, economic and cultural center of China and is experiencing severe haze pollution events frequently. It was found that organic matters were the largest component (28.2%) in $PM_{2.5}$, followed by sulfate (15.1%) during 2004-2013 which was overtaken by nitrate (14.9%) after 2013. Each $PM_{2.5}$ source demonstrated significant seasonal and annual variations, due to changes in climatic conditions and anthropogenic activities. Future research on the impacts of these external factors is urgently needed. This review is expected to provide valuable advice and evidence for those fast-growing megacities like Beijing to identify and control their $PM_{2.5}$ related air pollution problems.

Keywords: Fine particulate matter ($PM_{2.5}$); Chemical compositions; Source identification; Seasonal and annual variations; Air pollution control

Nomenclature

AAS	Atomic absorption spectroscopy	PCA	Principal component analysis
CMB	Chemical mass balance	$PM_{2.5}/PM_{10}$	Fine/Respirable particulate matter
EC	Elemental carbon	PMF	Positive matrix factorization
ICP-AES/MS	Inductively coupled plasma-atomic emission spectrometry/mass spectrometry	SNA	SO_4^{2-}, NH_4^+ and NO_3^-
OC	Organic carbon	SOC	Secondary organic carbons
OM	Organic matter	VOC	Volatile organic compounds
PAH	Polycyclic aromatic hydrocarbon	XRF	X-ray fluorescence

Graphical Abstract
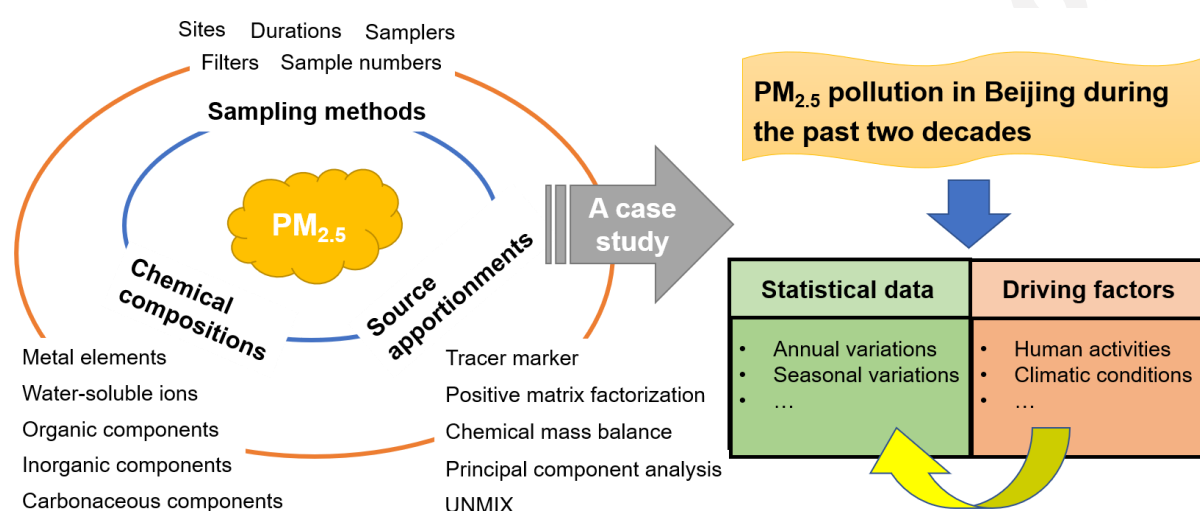
1. Introduction

Ambient air pollution is a top public health concern and has received significant attention worldwide in recent years (Petrova-Antonova et al., 2021). It is estimated that 4.2 million deaths are attributed to ambient air pollution worldwide every year (Huang et al., 2021c). Fine particulate matter ($PM_{2.5}$) is a key substance causing air pollution and endangering human health (Sosa et al., 2017; Zhao et al., 2018). $PM_{2.5}$ is a complex mixture of solid particulate matters, gases and water vapor in the air through a series of chemical reactions, which can be generated in both anthropogenic and natural activities (Cohen et al., 2010). Anthropogenic contributions mainly include motor vehicles, coal burning, industrial processes, cooking and biomass burning, while natural sources are usually from windblown soils, volcanic emissions, plant debris, sea spray and sandstorm (Manousakas et al., 2021). $PM_{2.5}$ has the characteristics of small size and large specific surface area (Li et al., 2020), leading to easy absorption of many toxic substances into human blood and lungs through the respiratory tract. Epidemiological studies showed that $PM_{2.5}$ is an important cause of asthma, chronic bronchitis, cardiovascular diseases, cancer and premature deaths (Perez et al., 2012). In addition, $PM_{2.5}$ has important impacts on atmospheric climates, such as visibility, photochemical pollution, cloud formation and rainfall (Chen et al., 2021; Wang et al., 2019).

To improve air quality, governments have set strict limits for $PM_{2.5}$ concentrations. **Table 1** gives the $PM_{2.5}$ standards in some countries, which are obtained from their official government websites. The World Health Organization (2021) has issued guidelines on criteria air pollutants, which sets an annual limit of 5 µg/m³ and a daily limit of 15 µg/m³ for $PM_{2.5}$ concentrations. In China, the latest $PM_{2.5}$ limits are 75 and 35 µg/m³ for annual and daily concentrations, respectively. Although these limits are higher than other countries, many studies indicated that $PM_{2.5}$ concentrations in China significantly exceeded the national

2

limits, especially in the fast-growing metropolises such as the Beijing-Tianjin-Hebei, Yangtze River Delta and Pearl River Delta regions (Yan et al., 2021; Feng et al., 2020).

Table 1. Typical air quality standards for $PM_{2.5}$ in some countries.

Country/Region	Daily limits ($\mu g/m^3$)	Annual limits ($\mu g/m^3$)
World Health Organization	15	5
European Union	-	20
US	35	12
Japan	35	15
India	60	40
China	75	35
Brazil	25	10
Russia	35	25
Bangladesh	65	15
Pakistan	35	15
Australia	25	8
Canada	27	8.8

Accurate identification of possible sources of $PM_{2.5}$ is the prerequisite for developing effective policies and control measures to improve air quality. Sampling, elemental and ions analysis, and source contributions are the major steps of source apportionment of $PM_{2.5}$ (Pui et al., 2014). Sampling is the first step after determining the sampling site. Different areas, including urban and suburban sites, are chosen to collect air samples. Quartz glass and Teflon filters are the most commonly used samplers. Samplers could be divided into high-, medium-, low- and mini-volume types (Yang et al., 2016). $PM_{2.5}$ is a complex mixture including heavy metal elements, water-soluble ions, organic matters and carbonaceous aerosols (Boman et al., 2013; Onat and Stakeeva, 2013). Resolving the chemical compositions of $PM_{2.5}$ is the key to analyze its sources (Karakas et al., 2017). Trace elements mainly refer to metal elements, among which heavy metal elements are extremely harmful to human health. Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES), X-ray fluorescence (XRF), Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Atomic Absorption Spectroscopy (AAS) are major tools for measuring trace metal elements (Lu et al., 2015; Manousakas et al., 2014). For water-soluble ions, SO_4^{2-}, NO_3^- and NH_4^+ (collectively known as SNA) account for the major mass fraction. Organic and elemental carbons (OC and EC) are major components of the carbonaceous composition. Regarding organic components, there are numerous organic species in $PM_{2.5}$. Despite significant researches on the compositions of organic aerosols in $PM_{2.5}$, there are still many species that are unknown and need further research.

After data acquisition, it is important to extract useful information from the data and relate $PM_{2.5}$ to its sources. Sources of $PM_{2.5}$ are complex, including both primary sources and secondary formations. $PM_{2.5}$ pollution are also affected by many factors, causing great difficulties to identify its sources. Practical analysis methods include receptor models, emission inventory models and air quality models. Among them, receptor models, based on multivariate statistical methods, are the most widely used (Hopke, 2016). Each receptor model has its respective limitations such as heavy dependence on accurate source profiles or sample capacity (Belis et al., 2020). New source identification methods were developed recently, such as comprehensive model methods (Wang et al., 2021) and molecular labeling techniques (Ikemori et al., 2021). However, their applications are limited and require further research.

Numerous studies about $PM_{2.5}$ pollution in Beijing were reported in recent years, and some efforts were made to review and categorize them. However, previous reviews mostly focused on the contrastive analysis of $PM_{2.5}$ concentrations, compositions and sources across different areas in China, with Beijing being only one of the sampling areas. He et al. (2017) reviewed the $PM_{2.5}$ concentrations in different regions of China from 2005 to 2016. The found that the highest levels of $PM_{2.5}$ were in the northern and northwestern regions, in particular Beijing. Similar results were also reported by Gautam et al. (2019) and Tao et al. (2017). Zhang et al. (2017a) reported that coal combustion, dust and biomass burning were the main sources of $PM_{2.5}$ in North China based on chemical speciation results from 31 cities and source apportionment results from 21 cities. However, dedicated reviews on $PM_{2.5}$ characterization in Beijing are relatively rare. The only review was conducted by Lv et al. (2016), which summarized studies on ground-

based observations and source apportionment results during 2000-2012 in Beijing. They also compared the PM$_{2.5}$ characterization in summer and winter with the consideration of diurnal variance, but the information about methods of sampling and source apportionments were very brief. With the increase of observation studies in recent years, as well as source apportionment models, the need for a comprehensive review on PM$_{2.5}$ characterization and modelling in Beijing is becoming conspicuous.

This paper aims to review the methods of sampling, chemical compositions and source apportionments of PM$_{2.5}$ and their latest applications in Beijing. The remaining of this review is organized as follows. Firstly, section 2 describes the scope of this review and the selection of literature. Secondly, section 3 introduces the sampling and chemical composition methods. Then, section 4 presents the source contribution methods, including tracer markers, calculation principles of typical receptor models, and their advantages and limitations. Finally, the annual and seasonal variations of chemical compositions and sources of PM$_{2.5}$ pollution in Beijing during the past two decades are discussed to highlight the correlations between natural factors and human activities. This review is expected to provide useful inspiration for the identification of PM$_{2.5}$, as well as some suggestions for its control strategies in megalopolises.

2. Methodology

In the process of collecting and identifying relevant studies, an extensive search for peer-reviewed publications about PM$_{2.5}$ chemical compositions and source identifications in Beijing was conducted on Web of Science. Multi-level filters were adopted in this process to select the most appropriate publications. The keywords of "PM$_{2.5}$" OR "fine particulate matter" were used to identify the research subject, and connector "AND" was used to prescribe a limit to the study site, "Beijing" OR "Bohai rim". The keywords of "chemical composition" OR "source contribution" OR "source apportionment" OR "source identification" OR "sampling method" OR "receptor model" were then used to determine the scope of research. The range of publication years was limited to from 2000 to 2021. Since there may be some deviations in the retrieval process, these retrieved literature were then screened manually by checking the titles, abstract and keywords. Some studies on the effects of PM$_{2.5}$ on human diseases and ecological changes were excluded, because they were out of the scope of this article. In addition, using the same set of data as other cited studies was not allowed. Applying these exclusion criteria, about 150 articles with independent measurements or models were processed and synthesized in this review.

3. Sampling and chemical compositions of PM$_{2.5}$

3.1. Sampling methods

Urban area was the most used for air quality monitoring, accounting for over 80% of published studies (**Table S1**). The monitoring sites are required to be open areas such as roofs and playgrounds. Future works are needed on suburban sampling sites to better understand the compositions and source contributions of PM$_{2.5}$. A complete sampler consists of selective filter, nitric acid decomposition solution, materials for adsorbing PM$_{2.5}$ and flow controller. The mass concentrations of PM$_{2.5}$ could be obtained by weighing the sampler before and after sampling. Teflon was a widely used filter material, whose sampling time generally lasts 24 hours or longer under the condition of 20 ℃ and 40% relative humidity. Electronic microbalances with a 1 μg sensitivity were widely used to measure the mass of PM$_{2.5}$. In addition to the gravimetric method, beta attenuation and tapered element oscillating microbalance were also commonly used for weighing PM$_{2.5}$. Their differences are compared in **Table S2**. Ion chromatograph, carbonaceous analyzer, ICP-MS were mainly used to obtain chemical compositions of PM$_{2.5}$. However, the differences in sampling instruments and methods, as well as the meteorological variations (temperature, wind speed and humidity) and human factors, would cause deviations in PM$_{2.5}$ composition analysis and source identification. It is necessary to measure PM$_{2.5}$ concentration in long-term and real-time. In recent years, aerosol mass spectrometer and real-time measuring technology have been developed to assess the source contributions of PM$_{2.5}$ (Brown et al., 2013). A comprehensive design on sampling tools, guided by reliable numerical models, was found to be helpful to reduce the uncertainty of the source analysis of PM$_{2.5}$ (Youn et al., 2021). Therefore, many countries have set up standards in sampling methods for PM$_{2.5}$, such as U.S. Environmental Protection Agency (1999); European Standards (2014); and China Ministry of Environmental Protection (2013).

3.2. Chemical compositions

Obtaining quantitative information on chemical compositions of atmospheric aerosols is critical for understanding the physicochemical properties of $PM_{2.5}$ and tracing their origins (Antony Chen et al., 2002). $PM_{2.5}$ consists of complex elements and chemical matters, including inorganic and organic components, water-soluble ions, and carbonaceous aerosols. Various methods and tools were used to measure the mass concentrations of each component in $PM_{2.5}$. **Table 2** summarizes the key chemical components in $PM_{2.5}$ and their measuring methods. For instance, Li et al. (2009) adopted a trace GC-MS spectrometer and an HP-5MS capillary column to measure organic components in $PM_{2.5}$. Gao et al. (2016) applied a non-dispersive infrared detector to analyze the characteristics of OC and EC in $PM_{2.5}$. The concentrations of six metal elements (Al, Zn, Cu, Pb, As, Cd) were measured and analyzed by ICP-AES (Yang et al., 2016).

Table 2. Measuring methods for different chemical components of atmospheric aerosols.

Chemical components	Measuring tools	Chemical species	Refs.
Inorganic components	XRF	Al, As, Ba, Br, Ca, Cl, Co, Cr, Cu, Fe, Ga, K, Mg, Mn, Mo, Na, Ni, P, Pb, Rb, S, Sb, Se, Si, Sr, Sc, Ti, V, Zn	(Gupta et al., 2021; Bilo et al., 2018; Shaltout et al., 2018; Dallmann et al., 2014; Mazaheri et al., 2013; Zhang et al., 2008)
	ICP-AES	Al, As, Ba, Bi, Br, Ca, Cl, Cd, Co, Cr, Cu, Eu, Fe, Ge, K, Mg, Mn, Na, Ni, P, Pb, S, Sb, Sc, Si, Sn, Sr, Ti, V, Zn	(González et al., 2017; Gao et al., 2016; Cheng et al., 2013a; Li et al., 2009; Wang et al., 2008)
	ICP-MS	Al, As, Ba, Ca, Cd, Co, Cr, Cu, Cs, Fe, K, Mg, Mn, Na, Ni, Pb, Rb, Sr, Sn, Sb, Ti, V, Zn	(dos Santos Souza et al., 2021; Yang et al., 2016; Huang et al., 2017; Hu et al., 2010; Song et al., 2006b)
	AAS	Al, As, Ca, Cd, Cr, Cu, Ni, Na, K, Mg, Mo, Mn, Pb, Fe, Sn, V, Zn	(Polezer et al., 2020; Shaltout et al., 2014)
	PIXE	Al, As, Br, Ca, Cr, Cu, Fe, Mn, Ni, P, S, Sc, Se, Si, Ti, V, Zn	(Yang et al., 2020; Waheed et al., 2012; Zheng et al., 2005)
Water-soluble ions	IC, AAS	Cl^-, F^-, SO_4^{2-}, NO_3^-, $C_2O_3^{2-}$, PO_4^{3-}, NO_3^-, $HCOO^-$, $CH3COO^-$, Ca^{2+}, Mg^{2+}, Na^+, K^+, NH_4^+	(Huang et al., 2020a; Huang et al., 2017; Cheng et al., 2013a; Guo et al., 2009; Antony Chen et al., 2002)
Carbonaceous compounds	TOT, TOR	OC, EC	(Fang et al., 2021; Dallmann et al., 2014; Timko et al., 2014; Guo et al., 2009; Wang et al., 2009a, 2008)
Organic compounds	GC-MS	N-alkanes, PAHs, SFA, UFA, Fatty alcohol, Saccharides, Polyatomic acid and Polyhydric alcohols, Steroid and Phenols, Terpenoids	(Lyu et al., 2019; Cropper et al., 2017; Dallmann et al., 2014; Han et al., 2010; Kong et al., 2010; Wang et al., 2009a; Zhang et al., 2007; Wang et al., 2005)

Notes: Some data came from Ref. (Zheng et al., 2014); IC: ion chromatograph; PIXE: proton-induced X-ray emission spectrometer; TOT/TOR: thermal optical transmittance/reflectance.

Inorganic components in $PM_{2.5}$ include metal elements such as Sb, As, Cd, Fe, Ba and Co, which are extremely harmful to human health. It was estimated that 3%-5% of global lung cancer deaths were caused by $PM_{2.5}$ air pollution since 2000 (Fang et al., 2013), mainly because $PM_{2.5}$ surface absorbs many harmful substances and could easily enter human body through respiratory tract (Feng et al., 2016). Metal elements are appropriate tracers to identify $PM_{2.5}$ sources. For example, crustal elements (e.g. Al, Ca, Si, K and Fe) are mainly from soil dust and trace elements (e.g. Cr and Ni) are mainly from industry (Zhao et al., 2021).

Water-soluble ions are major components in $PM_{2.5}$, including SNA, $C_2O_3^{2-}$, PO_4^{3-}, NO_3^-, MSA, $HCOO^-$, $CH3COO^-$, Ca^{2+}, Mg^{2+}, Na^+, and K^+. Among them, SNA are the most important components, which are generated by reactions of nitrogen oxides and sulfur oxides (Yin et al., 2014). The concentrations of SNA in $PM_{2.5}$ are greatly influenced by seasonal factors (Voutsa et al., 2014). Through ions and trajectory cluster analysis, Yang et al. (2015) suggested that SNA accounted for 81.2%, 78.5%, 74.6% and 76.3% of $PM_{2.5}$ in spring, summer, autumn and winter, respectively. Yao et al. (2002) conducted a one-year study on the chemical characteristics of $PM_{2.5}$ in Beijing and Shanghai, China, suggesting that SNA were the major composition (81%-85%) in $PM_{2.5}$ for both cities. The minority water-soluble ions in $PM_{2.5}$ (e.g. K^+, Na^+, Ca^{2+}, Mg^{2+} and Cl^-) also have significant impacts on the environment and human health (Deshmukh et al., 2013).

Considerable parts of PM$_{2.5}$ are composed of carbonaceous aerosols like OC (primary or secondary emissions) and EC (mainly from incompletely burning). Carbonaceous aerosols have various origins including human activities (e.g. traffic exhaust and coal burning), biological sources (e.g. pollen grains and plant debris) and secondary sources. Feng et al. (2014) showed that the average EC concentrations were 3.8 ± 2.3 μg·m^{-3} in 2010 and 3.3 ± 2.1 μg·m^{-3} in 2011 at an urban site in Shanghai, whose production was directly related to the human lifestyle. It should be noted that the appearance of EC would adversely affect the climate, environment and human health (Hand et al., 2013). EC is also known as black carbon due to its strong absorption of sunlight (Song et al., 2014). Automobile exhausts are important sources of EC in PM$_{2.5}$. Therefore, EC could be used as tracers for primary combustion emissions. The ratio of OC to EC indicated the formation of secondary organic aerosols. Huang et al. (2014) measured the hourly EC and OC during 2011-2012 in Hong Kong. They suggested that traffic emissions dominated EC emissions. EC concentrations showed no seasonal trends but high correlations with the traffic flows and NO$_x$ concentrations, especially in peak traffic hours. Souza et al. (2014) found that the average OC/EC ratio was greater than 2 (2.3-2.8) and had a good correlation (R=0.6-0.8) with PM$_{2.5}$ and PM$_{10}$. OC includes primary and secondary organic carbons (SOC), which are produced from emission sources directly and different physical and chemical reactions between precursors and other substances in the air, respectively. Under certain conditions, OC would be converted to organic matter (OM), with conversion factors of 1.95 and 2.05 for suburban and urban sites, respectively (Bressi et al., 2013).

Organic compounds are also abundant in PM$_{2.5}$ and mostly toxic. Among them, polycyclic aromatic hydrocarbons (PAHs) were the most widely studied, which were formed in incomplete combustion of fossil fuels and thermal decomposition of biomass (Li et al., 2013). The annual average concentrations of PAHs varied from tens to hundreds of ng·m^{-3} in the air. However, PAH concentrations near chemical factories may be much higher (Goldstein and Galbally, 2007). Benzo[b]fluoranthene, benzo[e]pyrene and phenanthrene account for the major mass of PAHs, with probabilities higher than 10^{-7} of causing cancer (Wu et al., 2014). SO$_2$ and volatile organic compounds (VOCs) (i.e. saturated, unsaturated, or aromatic hydrocarbons) have significant influences on the formation of atmospheric aerosols (Zhang et al., 2012). Other organic components of PM$_{2.5}$ include phthalate acid esters, secondary organic components, oxygenated volatile organic compounds and organic nitrogen (Samy and Hays, 2013). Although great efforts have been made to quantify the organic components of PM$_{2.5}$, there are still a considerable proportion of organic matters and molecules (30%~60%) that are not fully identified yet (Wu et al., 2020).

4. Source contribution of PM$_{2.5}$

Identifying the sources of PM$_{2.5}$ and determining their contributions have important influences on policy making to mitigate air pollution. Various models and tracer techniques were adopted to quantify the source contributions of PM$_{2.5}$. For example, Zhang et al. (2017b) reported that residential coal combustion accounted for 46% of PM$_{2.5}$ in severe haze events in the Beijing-Tianjin-Hebei region and even higher during the winter period, which provided critical information for effective and efficient control of air pollution in the concerned region.

Methods for identifying source contributions of PM$_{2.5}$ include emission inventory models, diffusion models, receptor models and comprehensive analysis. Among them, receptor models are the most widely used, although they have certain uncertainties since source contributions are vulnerable to many factors such as uncertainties of chemical composition measurements and secondary sources. Depending on the statistical method, receptor models can be divided into positive matrix factorization (PMF), factor analysis, principal component analysis (PCA), chemical mass balance receptor (CMB) and UNMIX models. New models (e.g. CMB-MM and CMBLGO) were also developed to reduce the apportionment uncertainties, as well as new approaches on source identifications such as specific species ratio, isotope labeling and backward trajectory methods. In this section, receptor models are introduced and discussed in detail.

4.1 Tracer markers

Table 3 gives the inorganic and organic tracers that were used for PM$_{2.5}$ source identification. Tracer markers are critical in identifying the source contributions, pollution events and chemical processes. Receptor models were usually combined with tracer markers to determine specific sources of PM$_{2.5}$, which could not be identified directly by receptor models. Yang et al. (2005b) used Ca and Al as tracer elements to determine the source contributions of PM$_{2.5}$ from crust in Beijing and Shanghai. They found that artificial

6

sources increased the Ca concentrations in PM$_{2.5}$. Wang et al. (2007) compared the tracer performance of CH$_3$Cl, CH$_3$CN, acetonitrile, levoglucosan and K$^+$ in identifying sources of biomass burning. They found that acetonitrile and levoglucosan were better than K$^+$ because similar concentrations of K$^+$ already existed in other emission sources. Zhou et al. (2017) adopted organic molecular markers and CMB model to ascertain major PM$_{2.5}$ sources, and identified five sources, namely traffic, biomass burning, cooking and natural gas burning. Yao et al. (2002) utilized SNA as tracers to identify the secondary source contributions of PM$_{2.5}$. They found that SO$_2$ was the major source of sulfate in winter due to the low ratio of SO$_4^{2-}$/SO$_2$ (0.27) in Beijing and Shanghai, indicating that stationary sources were the key sources of PM$_{2.5}$.

Table 3. Inorganic and organic tracers used in PM$_{2.5}$ source identification.

Tracer markers		Source categories	Refs.
Inorganic	SO$_4^{2-}$, NO$_3^-$, NH$_4^+$	Secondary aerosol	(Liu et al., 2017; Hu et al., 2014a; Wang et al., 2005)
	CaSO$_4$	Soil or road dust	(Popovicheva et al., 2019; Liu et al., 2005)
	K$_2$SO$_4$	Biomass burning	
	Ni, V	Residual oil combustion	(Guo et al., 2009; Ho et al., 2006)
	As, Cr, Cu, Fe, Ni, Mn, Pb, Sb, Zn	Steel production	(Hennigan et al., 2019; Lage et al., 2016; Yu et al., 2011)
	As, Ba, Br, K, Ni, Cd, Co, Cu, OC, Mn, Zn, Pb	Vehicle emission	(Hama et al., 2021; Yu et al., 2011; Han et al., 2010; Guo et al., 2009; Ho et al., 2006)
	Al, Ca, Mg, Fe	Construction and dust	(Kong et al., 2010)
	Na$^+$, K$^+$	Sea salt	
Organic	Benzo[k]fluoranthene, chrysene	Coal combustion	(Turap et al., 2018; Wang et al., 2014a)
	CA, HGA, 3-hydroxy-4, HDMGA, MBTCA	Secondary organic aerosols	(Li et al., 2018; Feng et al., 2013)
	Levoglucosan	Biomass burning	(Weichenthal et al., 2017; He et al., 2006; Gu et al., 2010)
	Cholesterol, β-sitosterol	Kitchen emission	(Xu et al., 2020; Gu et al., 2010; He et al., 2006)
	N-alkanes, triterpanes, phenanthrene, fluoranthene, pyrene, BghiP, IcdP	Vehicle emission	(Zhang et al., 2021b; Wang et al., 2014a; Feng et al., 2006)
	N-alkane (C$_{25}$-C$_{34}$)	Vegetative detritus	(Park et al., 2021; Al-Naiema et al., 2018)
	Hopanes	Fossil fuel combustion	(Tian et al., 2021; He et al., 2006)

Notes: CA, cispinonic acid; HGA, 3-hydroxyglutaric acid; HDMGA, 3-hydroxy-4, 4-dimeth ylglutaric acid; MBTCA, 3-methyl-1,2,3-butane-tricarboxylic acid; BghiP, benzo[g,h,i]perylene; IcdP, indeno[1,2,3-cd]pyrene.

4.2. Receptor models

Receptor models were the most popular method in source apportionment of PM$_{2.5}$. CMB model requires local source profiles to determine the primary sources, while PMF model identifies source distributions without any prior knowledge of source types (Gao et al., 2013). Thus, PMF model is currently the most frequently used model due to its convenience and practicability. However, source apportionment from receptor models is usually rough mainly because it is always affected by many complicated factors, such as meteorological conditions, spatial and temporal variations, and regional emissions. Meanwhile, the formation of PM$_{2.5}$ undergoes complex atmospheric chemical reactions (Balachandran et al., 2013), making it difficult to distinguish primary and secondary sources. Therefore, there are non-ignorable uncertainties in the process of quantifying the source contributions of PM$_{2.5}$. Reducing the uncertainties of receptor models and improving the reliability of measurements require further research.

4.2.1. PMF model

Over one-third of published studies after 2000 utilized PMF model to identify PM$_{2.5}$ sources in China (Engelbrecht et al., 2014) and some typical applications are summarized in **Table S3**. PMF is a bilinear

model which decomposes the predicted concentration matrix as multiplication of factor profile and contribution matrix. The measured concentration matrix can be presented as (Drosatou et al., 2019):

$$x_{ij} = \sum_{k=1}^{q} g_{ik} f_{kj} + e_{ij} \tag{1}$$

where x_{ij} is the measured concentration of j component at i sampling moment; g, f and e are the individual contributions, factor profiles and residuals of the analysis, respectively; q is the number of factors. Then, PMF attempts to modulate the factor profiles, making the predicted concentration matrix close to the measured one. In mathematical realization, this step is to minimize the objective function Q:

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \left(\frac{e_{ij}}{u_{ij}} \right)^2 \tag{2}$$

where u_{ij} is the data uncertainty determined by factor profiles and their contribution matrix.

The original PMF model utilized an alternating minimum iteration method which had a slow convergence rate. A faster algorithm was developed by computing factor and contribution matrices simultaneously (PMF 2.0). More innovative features, such as outlier detection, missing value correction, uncertainty estimation and input data preprocessing tools, were added into the PMF model. The latest PMF 5.0 model (U.S. Environmental Protection Agency, 2015a) further improved the convergence speed with a conjugate gradient algorithm (Belis et al., 2013). It is worth mentioning that accurately determining the number of optimal factors and the relationships of sources and factors will still be the optimization direction of PMF model in the near future.

4.2.2. CMB model

CMB accounted for about 20% of PM$_{2.5}$ source identification studies in China since 2000 (typical applications are given in **Table S4**). CMB model determines source contributions by using the least-square method of variance based on local source profiles. In the least-square method, the weight relationship for PM$_{2.5}$ and local source profiles is described by Eq. (3):

$$(w_i)_{mn} = \frac{1}{\delta_m^2 + \sum_{n=1}^{q} \sigma_{mn}^2 f_n^2} \tag{3}$$

where δ_m is the uncertainty of PM$_{2.5}$ in sampling tools, σ_{mn} is the uncertainty of substance n in the mth source in sample data. CMB determines source contributions by the following steps: 1) determine the major PM$_{2.5}$ sources; 2) select the chemical components in samplers and calculate their mass concentrations; 3) estimate the contributions of each chemical component to source profiles; 4) evaluate uncertainties and errors between PM$_{2.5}$ concentrations and local source profiles; and 5) output final results.

Different from PMF, the accuracy of CMB is susceptible to local source profiles, changes in external conditions and sample numbers. The local source profile is a required input for CMB. Therefore, accurate pre-knowledge of local PM$_{2.5}$ sources is needed to ensure reliable identification results. Further, all possible relevant emission sources should be considered to analyze the uncertainties between PM$_{2.5}$ and local source profiles. There are many different ways to develop source profiles, where dilution and thermal decomposition of samples are the most frequently used methods (Chow et al., 2004). Detailed information on methods of developing profiles from different sources in various regions can be found in (Fine et al., 2004; Schauer et al., 2002).

A comprehensive source profile database plays a critical role in the application of CMB. Local source profiles from different regions could offer significant indications for the identification and quantification of major sources of PM$_{2.5}$. In recent years, standard source profile databases have been proposed for Europe (i.e. SPECIEUROPE) and the United States (i.e. SPECIATE) (Pernigotti et al., 2016; Simon et al., 2010; U.S. Environmental Protection Agency, 2015b; Wang et al., 2015c). However, China has not established its unified source profile database and local source profiles are relatively rare. It is very important to develop standards for sampling, chemical composition identification and quantification to establish source profiles in different regions of China.

4.2.3. PCA

PCA applies statistical methods to transform complex variables into a series of relatively simple data and then to determine quantitative factors of major sources on PM$_{2.5}$. The core step in PCA is the dimension reduction process, which converts the original sample set into an indicator set by Eq. (4):

$$X = \begin{pmatrix} x_{11} & \cdots & x_{1p} \\ \vdots & \ddots & \vdots \\ x_{n1} & \cdots & x_{np} \end{pmatrix} \rightarrow \begin{cases} z_1 = L_{11}x_1 + L_{12}x_2 + \ldots + L_{1p}x_p \\ \qquad \ldots\ldots \\ z_m = L_{m1}x_1 + L_{m2}x_2 + \ldots + L_{mp}x_p \end{cases} \quad (4)$$

where n is the number of samples, m is the number of elements, X is the original variable indicator, z_m is the new indicator after reducing the dimension ($m<p$), L_{mp} is the corresponding load factor on each chemical species, and z_1 and z_2 are the first and second main components, respectively. Then PCA adopts two steps to determine the source contributions of $PM_{2.5}$. Firstly, the collected chemical sample data is converted into a dimensionless standard value by Eq. (5):

$$q_{ij} = \frac{c_{ij} - \overline{c}_j}{\delta_j} \rightarrow zij = \sum_{k=1}^{p} p_{ik}m_{kj} \quad (5)$$

where c_{ij} is the concentration of the jth element in the ith sample, $\overline{c_j}$ is the average concentration of element j in the samples, δ_j is the standard deviation, k represents the number of sources, p_{ik} is the load factors, and m_{kj} represents emission factors in samples (Jain et al., 2018).

Secondly, the correlation coefficient matrices are calculated based on the sample data, the component and cumulative contribution rates. Generally, when the eigenvalue of the cumulative contribution is over 85%, the previous complex variables could be replaced by fewer comprehensive indicators. The most critical part is to determine the distributions of each major component to potential sources in PCA. Contrary to the PMF method, PCA does not directly assess the uncertainties of data. Noises due to data uncertainties are incorporated into the principal components (Paatero and Hopke, 2003). In short, the collinearity of the source profiles may introduce redundant principal components in the PCA process.

A number of PCA applications on $PM_{2.5}$ source identification were reported. Viana et al. (2006) determined seven $PM_{2.5}$ sources by combining PCA with the multi-linear regression method. They reported that motorway traffic contributed more $PM_{2.5}$ than local traffic. Gupta et al. (2018) collected $PM_{2.5}$ samples in India and used molecular marker techniques and PCA to determine the source contributions of $PM_{2.5}$. They found that road transport was a larger $PM_{2.5}$ source than other human activities. Bruno et al. (2008) analyzed the major $PM_{2.5}$ sources in Bari with the absolute principle component model, suggesting that road traffic is less influential to $PM_{2.5}$ formation than secondary sources. Amato et al. (2010) collected samples of PM_{10} at an airport. PCA modeling showed that crust was the largest source of PM_{10} (38%), while OC, EC and secondary inorganic aerosols accounted for 25%, 20% and 6%, respectively. Negral et al. (2008) monitored particulates at a suburban station in Spain. They found that shipyard emissions were well correlated with the mass concentrations of Ci and Ni elements, and secondary aerosol had a similar relationship between Ni and V elements. These suggested that fossil oil burning had a great contribution to PM_{10} and the sources of $PM_{2.5}$ were quite different from PM_{10}.

4.2.4. UNMIX model

A novel multi-receptor model (UNMIX) based on factor analysis was developed by Henry (2003) to address the problem of $PM_{2.5}$ source apportionment without local source profiles. UNMIX model applies three key assumptions, including 1) contributions of unknown $PM_{2.5}$ sources are a linear combination of various source components with receptor points, 2) source profiles and contributions are non-negative, 3) small minority samples have no contribution for each specific source. UNMIX model treats sample data as a multidimensional space. Source contributions would be identified by reducing the dimension and finding the right edge of the data with single-valued numerical analysis.

There are four major steps in utilizing UNMIX model. First, particle samples were collected to analyze chemical compositions. Next, characteristics of 4-8 pollutant sources were found with maximum variance factor analysis, and to further correct the model. Then, the number of pollutants was increased to calculate the source contributions, as well as the uncertainty of each pollutant. Finally, solutions were validated and supplemented with local source information before outputting the ultimate results. The reliability of ultimate results depends on whether the sample data satisfied the assumptions of UNIMX model. Opposite results to other receptor models would be generated when the data does not satisfy the assumptions.

UNMIX model (the latest version is UNMIX 6.0) (U.S. Environmental Protection Agency, 2015c) were frequently used in $PM_{2.5}$ source identification. Herrera Murillo et al. (2012) used UNMIX model to identify $PM_{2.5}$ sources under conditions of unknown emission source catalogs and profiles in Salamanca. They determined four main sources (i.e. secondary aerosol, heavy fuel burning, biomass combustion and

brick contribution) and indicated that local sources were dominant to PM$_{2.5}$. Hellén et al. (2003) studied the sources of hydrocarbons with UNMIX model in Helsinki. They suggested that the major sources of C$_2$-C$_6$ consisted of gasoline combustion (54%) and long-distance and local regional sources (37%). Besides, small contributions came from city gas (2%), solvents (3%), biological compounds (1%) and diesel exhaust (0.2%). Hu et al. (2006) used UNMIX model to analyze the PM$_{2.5}$ sources near an intercontinental highway. They found that combustion, regional second sulfate and traffic exhaust were the major contributing sources, and PM$_{2.5}$ concentrations were sensitive to seasonal factors except for traffic exhaust.

4.3. Comparison and integration of receptor models

Table S5 compares the four main receptor models introduced in Section 4.2. As a qualitative receptor model, PCA model is simple to use. The pollution source could be preliminary identified by PCA model on statistical software such as SPSS or Excel. However, the number of identified sources from PCA model is limited, and their contributions cannot be quantified. CMB model was proposed by Miller et al. (1972) for analyzing the sources of atmospheric PM. It is important to note that CMB model calculates source contribution by using the effective variance least-square method which is based on local source profile and characteristics of receptor point component. Generally, traditional CMB model may get relatively clear emission source catalogs without strict requirements on the number of samples. However, CMB model relies on accurate profiles of local sources, and it is unable to distinguish between different emission sources with similar chemical compositions (i.e. collinear problem). Factor analysis methods have been widely used in source apportionment without local source profiles. PMF model, a new method for resolving PM source contributions based on the traditional factor analysis method, was developed by Paatero and Tapper (1993). Compared to CMB model, PMF model does not require exact source profiles but needs tracers that are indicative of source contribution and a large amount of sample data (generally >100 samples). There are certain subject activities and uncertainties in the use of PMF model. UNMIX model could identify the sources and contributions directly by the concentration data of samples, without any complex transformations. The reliability of analytical results is displayed directly in the outputs, which would contribute to the selection of valid species. Due to the high dependence on selected species, UNMIX model has a rigorous requirement for data samples. The data should be of high quality (above detection limit) and have a low percentage of missing values (below 75%). In addition, a large sample demand also increases the difficulty in its practice.

The uncertainties from local source profile, meteorology and chemical mechanism of the atmosphere have important impacts on the robustness of source identifications with receptor models. To overcome the limitations mentioned above, integrated models were proposed recently for better accuracy and reliability. Song et al. (2006a) compared the performance of PCA and UNMIX models. They reported that both models agreed with previous results from PMF and CMB models. Callén et al. (2009) used integrated receptor models to analyze PM source contributions in Zaragoza. They found that natural sources contributed more PM$_{10}$ (47%-75%) than anthropogenic sources (25%-39%). PCA, PMF and UNMIX models identified 8, 9 and 6 source catalogs, respectively. Jain et al. (2018) investigated the source contributions of PM$_{2.5}$ with PCA and UNMIX models, reconfirming that traffic exhaust, secondary aerosols, biomass combustion and soil dust were the key PM$_{2.5}$ sources in Delhi. Hu et al. (2014b) used multi-mixed source analytical model techniques to determine PM$_{2.5}$ source contributions and compared with previous studies using the same monitoring site. They showed that the new model could overcome the collinearity problem of a single receptor model, resolve sources of secondary products and reduce the uncertainties of quantified results.

5. Variations of PM$_{2.5}$ pollution in Beijing during the past two decades

5.1. Variations of chemical compositions

Beijing, the capital city of China and one of the largest megacities globally, experienced a rapid increase of haze and air pollution events in recent years, particularly in winter (He et al., 2018; Zhang et al., 2021a). The source appointment of air pollution in Beijing attracted significant attention. Among them, extensive studies on the chemical compositions of PM$_{2.5}$ were carried out at various monitoring sites in Beijing. **Fig. 1** summarizes the reported chemical compositions and the annual variations of three major PM$_{2.5}$ compositions (i.e. OM, EC and SNA) from 2004 to 2016 in Beijing. There are many kinds of OM in in PM$_{2.5}$, among which hydrocarbons (including alkanes, alkenes, aromatic hydrocarbons and PAHs) are the main components. In addition, there are nitrosamines, nitrogen-containing heterocyclic compounds,

ketones, quinones, phenols, acids etc. To minimize uncertainties, data were only derived from long-term (>3 months) sampling studies. As shown in **Fig. 1a**, OM is the largest component (20.4%-35.7%) of PM$_{2.5}$ during 2004-2016 in Beijing, which decreased from 2004 to 2011 and then remained stable after 2011. The second largest component is sulfate (11.4%-19.8%) during 2004-2013, followed by nitrate (17.5%-22.2%). However, nitrate overtook sulfate (17.5%-22.2%) after 2013. **Fig. 1b** shows that PM$_{2.5}$ was dominated by carbonaceous components (OM+EC) and SNA in Beijing from 2004 to 2016. In general, the proportion of OM+EC showed a downward trend from 2004 (40.1%) to 2016 (28.6%), while the proportion of SNA had an upward trend (32.6%-44.0%). OM+EC was the largest component of PM$_{2.5}$ before 2009, which was overtaken by SNA after 2009.
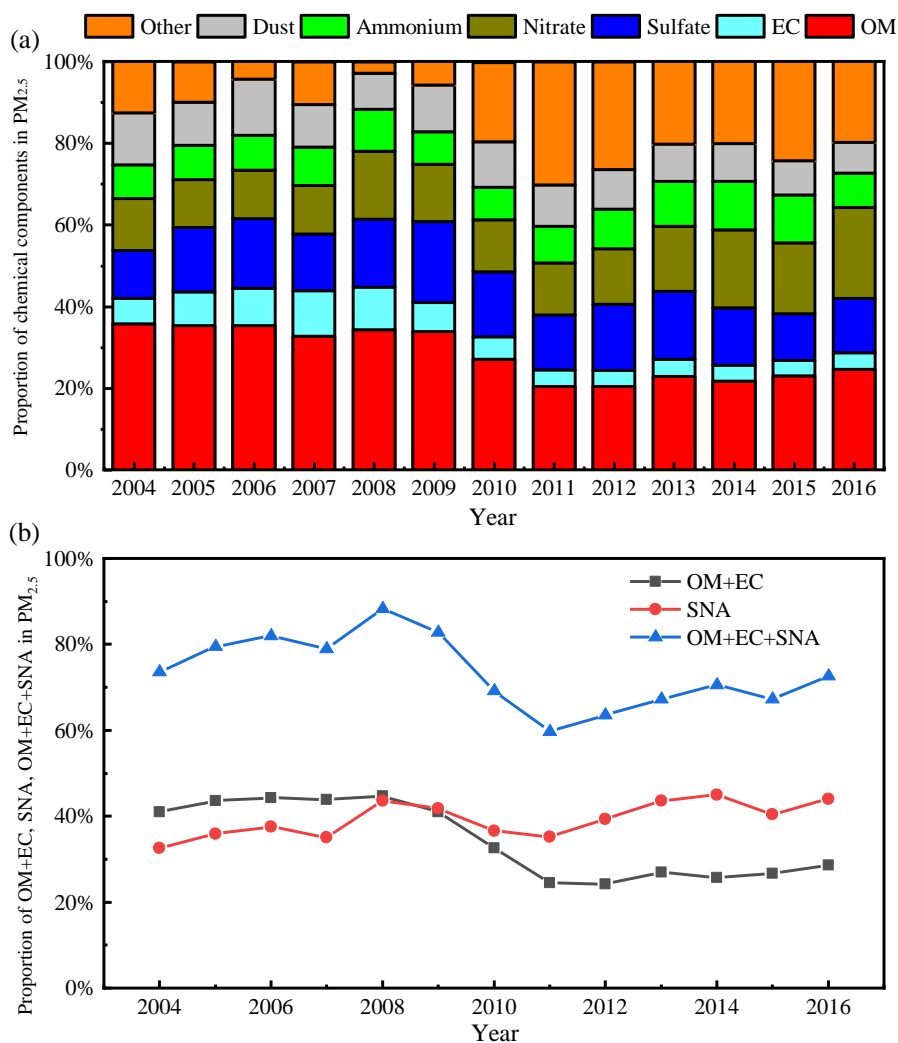

Fig. 1. Proportions of chemical components **(a)** and OM, EC and SNA **(b)** in PM$_{2.5}$ from 2004 to 2016 in Beijing. Data were from Refs. (Lang et al., 2017; Yu et al., 2011; He et al., 2011; Wang et al., 2009b).

Fig. 2 shows the OC and EC concentrations and OC/EC ratios during 2004-2018 in Beijing. The information about sample and chemical analysis are given in **Table S6.** OC concentration peaked in 2006 and then decreased during 2006-2012. The decreasing trend of OC may be resulted from the implementation of a series of strict emission controls during the 2008 Beijing Olympic Games (Wang et al., 2010). OC has two major sources, namely primary and secondary sources. Primary sources mainly refer to direct emissions including motor vehicles, coal combustion and biomass burning. Secondary sources are mainly the conversion of VOCs emitted by motor vehicles into OC via a series of complex chemical reactions (Wang et al., 2014b; Yang et al., 2005a). Improving fuel quality and transportation conditions are important measures to mitigate OC concentrations. It was found that biomass burning is another key source of OC, in particular in autumn and winter (Zhao et al., 2013; 2009). Developing relevant regulations to improve biomass combustion is helpful to reduce OC concentrations.

As illustrated in **Fig. 2**, the annual average EC concentration peaked in 2007 (12.0 μg/m^3), then declined from 2008 (8.4 μg/m^3) to 2012 (3.0 μg/m^3). Studies showed that incomplete combustion of fossil

fuels and biomass was an important source of EC (Zhang et al., 2013). The decrease of EC after 2007 was related to the continuous reduction of coal use in Beijing and the gradual improvement of fossil fuel combustion. Controlling biomass burning by relevant policies also helped reduce EC concentrations. Lang et al. (2017) reported that fossil fuels were replaced gradually by clean energy since 2007 in Beijing, which was likely another reason for the decrease of EC concentration. EC concentration dropped slightly during 2013-2015, which may be attributed to strict policies and regulations. Specifically, the government proposed a series of policies and regulations to promote comprehensive utilization of straw in 2013. Cheng et al. (2013b) found that EC and K (tracer element of biomass burning) concentrations were well correlated (R=0.94), further indicating that biomass burning is a key source of EC.

OC/EC ratios could be adopted to distinguish different combustion sources (Wang et al., 2009c). $PM_{2.5}$ is mostly from fossil fuel combustion (e.g. coal, oil and natural gas) when OC/EC is less than 0.4 (Wang et al., 2006). When OC/EC increases up to 1.1, traffic exhausts become the major source of carbonaceous components in $PM_{2.5}$ (Gonçalves et al., 2011). If OC/EC reaches 2 or more, a large amount of SOC would be formed, whose concentration increases with OC/EC ratio (Tian et al., 2015). As shown in **Fig. 2**, OC/EC ratios were relatively high during 2004-2018 in Beijing, with an average value of 3.4, indicating that there was significant SOC forming in $PM_{2.5}$. Especially from 2007 to 2018, OC/EC increased from 1.79 to 7.31, meaning that SOC pollution in Beijing was aggravated.
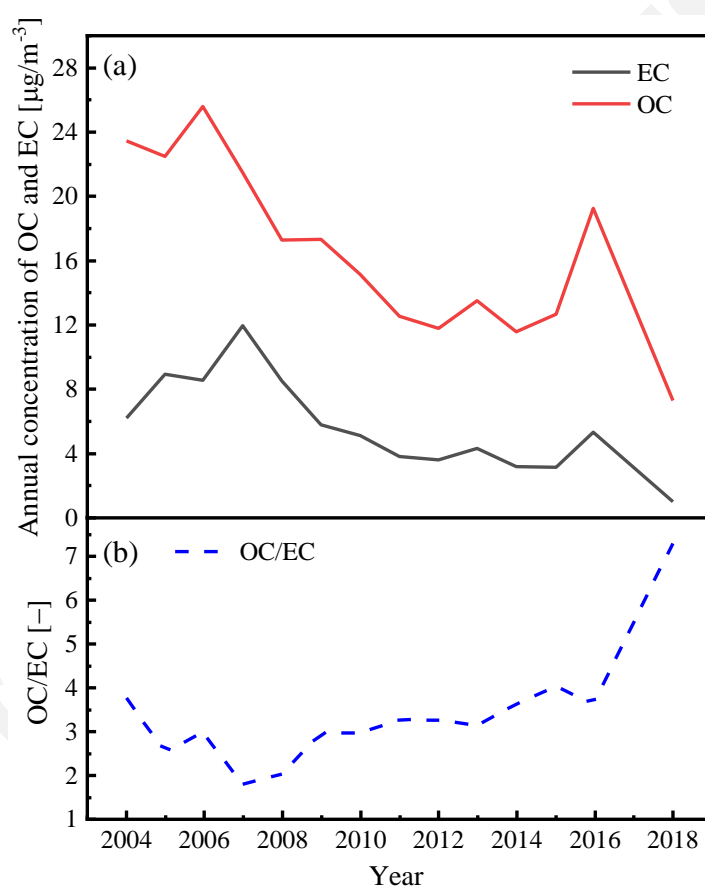

Fig. 2. Annual concentrations of OC and EC **(a)** and OC/EC ratios **(b)** from 2004 to 2018 in Beijing. Data were from Refs. (Huang et al., 2021b; Zhang et al., 2018; Lang et al., 2017; Wang et al., 2016b, 2015a; Zhang et al., 2013; Zhao et al., 2013; Yang et al., 2011; He et al., 2011; Zhao et al., 2009; Xu et al., 2007).

5.2. Variations of source contributions

Fig. 3 shows the annual average source contributions of $PM_{2.5}$ in Beijing from 2000 to 2018. Vehicle emissions (mainly gasoline and diesel combustion), dusts (including soil and construction dusts) and industrial emissions (mainly metallurgical industry) are reviewed. Some data (2012-2013 and 2017-2018) was from the official statistics of the Beijing Environmental Protection Bureau (BEPB). Such information is of great value for developing recommendations and measures to mitigate air pollution. For consistency, only the data from PMF method was discussed and compared in detail. Considering that $PM_{2.5}$ is susceptible to seasonal factors (Liu et al., 2018; Samy and Hays, 2013), source identifications in four seasons are presented in **Fig. 4**.

Fig. 3. Source contributions of PM$_{2.5}$ in Beijing during 2000-2018. Data were from Refs. (Song et al., 2006a; Yu et al., 2013; Zhang et al., 2013; Timko et al., 2014; Zhang et al., 2015; Zíková et al., 2016; Lv et al., 2016).

Fig. 4. Source contributions of PM$_{2.5}$ in Beijing from 2010 to 2018. Results with star (*) only considered fine organic aerosols. Data were from Refs. (Zheng et al., 2005; Song et al., 2007; Wang et al., 2009b; Zhang et al., 2013; Yu et al., 2013; Wang et al., 2015b; Yang et al., 2016; Zhang et al., 2016; Zíková et al., 2016; Zhang et al., 2018; Ji et al., 2018).

13

The average source contributions from vehicles, dusts, industry, biomass burning, coal combustion and secondary products from 2000 to 2018 were 14.3%, 13.9%, 10.7%, 7.6%, 15.9% and 31.6%, respectively. Secondary products, including secondary sulfates, nitrates and ammonium salts, were the largest source to the formation of $PM_{2.5}$. However, new desulfurization and denitration technologies spread rapidly because strict monitoring policy on polluting enterprises was implemented by the Beijing government in 2008-2009. Thus, the average contribution of secondary products after 2009 decreased to 27.3%, reaching a minimum of 20% in 2014. The secondary products were the highest in summer (41.7%) while spring, fall and winter were 34.7%, 27.6%, 31.2%, respectively. This was probably caused by the high temperature, strong radiation and high humidity during summer.

As the second largest $PM_{2.5}$ source, traffic emissions on average contributed 5.5% before 2010 but increased rapidly to 26% after 2010. This is closely related to the number of vehicles in Beijing, which increased 3.4 times from 2004 (1.8 million) to 2018 (6.1 million) (**Fig. S1**). After 2010, car ownership entered the saturation period (>5 million). Another important factor is the rise of cross-regional transportation. From around 2000, heavy industries, such as steel mills, car manufacturers and chemical plants, began to be gradually relocated from Beijing to mostly Hebei province. A typical example is the production of crude steel, which experienced a rapid growth in Hebei province from 56 to 180 million tons per year during 2004-2012 (**Fig. S2**). Therefore, the huge demand for industrial materials in Beijing relied on the supply from neighboring regions. The relocation of heavy industries suppressed the contribution of industrial emissions on $PM_{2.5}$ formation, which decreased by 6% during 2012-2018. On the other hand, motor vehicles became the highest contributor in summer due to high temperature and thermal radiation.

Another important source with an increasing trend is dust. The average contribution of dust on $PM_{2.5}$ was 13.2% before 2010 and increased to 14.7% after 2010. This was mainly related to changes in human activities such as urban construction. The area of built urban district in Beijing increased rapidly during 2004-2018, except for a sudden drop during 2009-2011 due to a change of statistical method (**Fig. S3**). The large-scale urban construction, coupling with the agglomerative effect of the population, led to the rise in the contribution of dust on $PM_{2.5}$. Seasonal variations in **Fig. 4** indicate that dust contributed much more $PM_{2.5}$ in spring than in other seasons. Natural causes include less rainfall and windier in spring, which are favorable conditions for dust to transport and suspend in the air.

As a major utilization method of solid fuels, biomass and coal combustion on average contributed 7.6% and 15.9% of $PM_{2.5}$, respectively. Main biomass fuels are agriculture wastes and woods. In autumn and winter, substantial biomass fuels were burned for waste disposal and heating in the peri-urban and suburban areas, leading to higher seasonal contributions of biomass burning in autumn (11.0%) and winter (12.4%). For a similar reason, central heating in winter burned a large amount of coal, leading to an obvious increase in the contribution of coal combustion in winter (27.6%) comparing with other seasons (i.e. 8.0% in spring, 4.4% in summer and 7.2% in autumn). Due to bans on straw burning by China Environmental Protection Administration (Huang et al., 2021a) and relocation of heavy industries, the contributions of biomass burning and coal combustion were on a down trend. The average contribution of biomass burning decreases to 6% after 2010, and coal combustion decreased from 22% in 2012 to only 3% in 2017.

Based on the above analysis of source contributions of $PM_{2.5}$ in Beijing, some suggestions on control strategies of $PM_{2.5}$ could be given. Vehicle emissions have become the largest contributor of $PM_{2.5}$ in cities now (Huang et al., 2022b). Some policies were introduced to mitigate the problem. Starting from 2020, the $PM_{2.5}$ emission limit of light vehicles in Beijing has been reduced to 3 mg/km (Beijing Municipal Ecology and Environment Bureau, 2019). Policies are also actively promoting the use of new energy vehicles powered by lithium batteries and fuel cells for both households and firms (Beijing Municipal Science and Technology Commission, 2018). Meanwhile, it is of the same level of importance to control the emissions from the huge numbers of existing in-use vehicles which are usually powered by fossil fuels and will remain on road for many years before they retire. Adopting the latest technologies to trace real-time $PM_{2.5}$ emissions of on-road vehicles offers valuable information for source identification and modelling. An example is the on-road remote sensing technology which could rapidly detect high-emitting vehicles for targeted emission control without interfering normal driving and realize significant roadside air quality improvements (Huang et al., 2020b; 2022a). Another important control is for secondary products, including solid fuel combustion. The most essential control strategy is to reduce the harmful elements in the fuel, like sulfur, nitrogen and mercury. The Beijing government has established substantial measures to implement this principle: over 60 industrial enterprises in urban area were stopped or limited to production in winter of 2017, and natural gas was promoted for industrial and residential sectors. As an important supplement,

promoting the centralized and clean combustion technology of biomass, such as biomass gasification technology, would efficiently decrease $PM_{2.5}$ emissions (Molino et al., 2016). From the point of view of renewable energy sources, adopting solar, ground and air source heat pumps, and other new technologies to replace coal for heating could also help reduce secondary products in winter (Carroll et al., 2020).

6. Conclusions and future directions in field

Air pollution, especially $PM_{2.5}$ pollution, continues to be a serious environmental problem due to the rapid economic growth and urbanization. This study provides a comprehensive review on the methods of sampling, chemical compositions and source apportionment of $PM_{2.5}$. An in-depth survey on the variations of $PM_{2.5}$ compositions and source apportionments in Beijing in the past two decades is conducted. The key conclusions are drawn as follows:

(1) Sampling devices have important influences on identification of $PM_{2.5}$ chemical compositions and source contributions. Quartz and Teflon filters are the most frequently used for collecting $PM_{2.5}$, and the accuracy should at least reach 1 μg to meet the requirement for weighing $PM_{2.5}$ samples. Inorganic components, water-soluble ions, carbonaceous components and organic components are the major components of atmospheric $PM_{2.5}$. Heavy metals in inorganic components can be easily adsorbed on the surface of $PM_{2.5}$, which can enter human lungs and cause great harm to human health. SNA is the major part of water-soluble ions, which is formed from secondary reaction of precursors in the air. OC, EC and OM are the major parts of the carbonaceous components. Organic species are abundant in $PM_{2.5}$ and mostly toxic except for PAHs. The knowledge about other organic species is still insufficient.

(2) The principles and applications of four typical receptor models (i.e. PMF, CMB, PCA and UNMIX) on $PM_{2.5}$ source appointment were discussed. CMB model relied on accurate profiles of local sources, while other models did not require exact source profiles but at the cost of higher uncertainties. In fuzzy source appointments, PCA and PMF models could identify more source catalogs than UNMIX model. Developing standard source profiles is of great importance for $PM_{2.5}$ identification, which is rare in most regions of China.

(3) Variations of $PM_{2.5}$ compositions and sources in Beijing were surveyed. OM is the most important component in $PM_{2.5}$ (28.2%), followed by sulfate (15.1%) during 2004-2013 which was overtaken by nitrate (14.9%) after 2013. OC/EC ratio increased from 1.79 to 3.71 during 2007-2016, meaning that SOC pollution was aggravated. Secondary products, coal combustion, vehicle exhaust, dust, industrial emission and biomass burning were the major sources of $PM_{2.5}$ during 2004-2018, with average contributions of 31.6%, 15.9%, 14.3%, 13.9%, 10.7% and 7.6%, respectively. The contributions of most sources decreased, except for vehicle exhaust and dust. Major influencing factors include growths of urban population, motor vehicles and construction, stricter environment policies, and relocation of heavy industries. Seasonal variations in source contributions were related to human activities such as central heating in winter, as well as climatic conditions such as wind and temperature.

(4) Based on the analysis in this paper, Beijing, a typical northern metropolis, should pay more attention on the $PM_{2.5}$ from on-road vehicles, secondary products and solid combustion. In addition to existing policies, promoting targeted emission control of on-road vehicles, cleaner combustion technologies of biomass and new heating technologies could greatly benefit the control of $PM_{2.5}$. In the future, more efforts should be made to clarify the influence of new transportation and industry technologies related to combustion, heating, air purification and construction on $PM_{2.5}$ characterization in the air. Regarding modelling, developing hybrid receptor models and coupling them with emission inventory models would be the focus of future research.

Supplementary information

Additional information about number of motor vehicles in Beijing (**Fig. S1**), production of crude steel in Hebei province (**Fig. S2**), urban population and area of built district in Beijing (**Fig. S3**), monitoring studies in Beijing (**Table S1**), comparison of PM$_{2.5}$ sampling methods (**Table S2**), PMF model applications (**Table S3**), CMB model applications (**Table S4**), comparison of main receptor models (**Table S5**), sampling and chemical analysis of PM$_{2.5}$ in Beijing (**Table S6**).

References

Al-Naiema, I.M., Yoon, S., Wang, Y.-Q., et al., 2018. Source apportionment of fine particulate matter organic carbon in Shenzhen, China by chemical mass balance and radiocarbon methods. *Environ. Pollut.* 240, 34–43.

Amato, F., Moreno, T., Pandolfi, M., et al., 2010. Concentrations, sources and geochemistry of airborne particulate matter at a major European airport. *J. Environ. Monit.* 12, 854–862.

Antony Chen, L.-W., Doddridge, B.G., Dickerson, R.R., et al., 2002. Origins of fine aerosol mass in the Baltimore–Washington corridor: implications from observation, factor analysis, and ensemble air parcel back trajectories. *Atmos. Environ.* 36, 4541–4554.

Balachandran, S., Chang, H.H., Pachon, J.E., et al., 2013. Bayesian-Based Ensemble Source Apportionment of PM$_{2.5}$. *Environ. Sci. Technol.* 47, 13511–13518.

Beijing Municipal Ecology and Environment Bureau, 2019. Beijing early implementation of the six motor vehicle emission standards. http://sthjj.beijing.gov.cn/bjhrb/index/xxgk69/zfxxgk43/fdzdgknr2/xwfb/851653/index.html (accessed 3.31.22).

Beijing Municipal Science and Technology Commission, 2018. The popularization and application of new energy automobile management approach. http://kw.beijing.gov.cn/art/2018/2/26/art_2386_2610.html (accessed 3.31.22).

Belis, C.A., Karagulian, F., Larsen, B.R., et al., 2013. Critical review and meta-analysis of ambient particulate matter source apportionment using receptor models in Europe. *Atmos. Environ.* 69, 94–108.

Belis, C.A., Pernigotti, D., Pirovano, G., et al., 2020. Evaluation of receptor and chemical transport models for PM$_{10}$ source apportionment. *Atmos. Environ. X* 5, 100053.

Bilo, F., Borgese, L., Wambui, A., et al., 2018. Comparison of multiple X-ray fluorescence techniques for elemental analysis of particulate matter collected on air filters. *J. Aerosol Sci.* 122, 1–10.

Boman, J., Shaltout, A.A., Abozied, A.M., et al., 2013. On the elemental composition of PM$_{2.5}$ in central Cairo, Egypt. *X-Ray Spectrom.* 42, 276–283.

Bressi, M., Sciare, J., Ghersi, V., et al., 2013. A one-year comprehensive chemical characterisation of fine aerosol (PM$_{2.5}$) at urban, suburban and rural background sites in the region of Paris (France). *Atmos. Chem. Phys.* 13, 7825–7844.

Brown, S.G., Lee, T., Roberts, P.T., et al., 2013. Variations in the OM/OC ratio of urban organic aerosol next to a major roadway. *J. Air Waste Manag. Assoc.* 63, 1422–1433.

Bruno, P., Caselli, M., de Gennaro, G., et al., 2008. Application of receptor models to airborne particulate matter. *Microchem. J.* 88, 121–129.

Callén, M.S., de la Cruz, M.T., López, J.M., et al., 2009. Comparison of receptor models for source apportionment of the PM$_{10}$ in Zaragoza (Spain). *Chemosphere* 76, 1120–1129.

Carroll, P., Chesser, M., Lyons, P., 2020. Air Source Heat Pumps field studies: a systematic literature review. *Renew. Sust. Energ. Rev.* 134, 110275.

Chen, W., Ren, J., Chen, T., et al., 2021. The impact of haze on photovoltaic systems: a case study, *Energ. Source. Part A*, article in press.

Cheng, S., Lang, J., Zhou, Y., et al., 2013a. A new monitoring-simulation-source apportionment approach for investigating the vehicular emission contribution to the PM$_{2.5}$ pollution in Beijing, China. *Atmos. Environ.* 79, 308–316.

Cheng, Y., Engling, G., He, K.-B., et al., 2013b. Biomass burning contribution to Beijing aerosol. *Atmos. Chem. Phys.* 13, 7765–7781.

China Ministry of Environmental Protection, 2013. Specifications and Test Procedures for PM_{10} and $PM_{2.5}$ Sampler. https://www.mee.gov.cn/ywgz/fgbz/bz/bzwb/jcffbz/201308/t20130802_256854.shtml (accessed 10.14.21).

Chow, J.C., Watson, J.G., Kuhns, H., et al., 2004. Source profiles for industrial, mobile, and area sources in the Big Bend Regional Aerosol Visibility and Observational study. *Chemosphere* 54, 185–208.

Cohen, D.D., Crawford, J., Stelcer, E., et al., 2010. Characterisation and source apportionment of fine particulate sources at Hanoi from 2001 to 2008. *Atmos. Environ.* 44, 320–328.

Cropper, P.M., Overson, D.K., Cary, R.A., et al., 2017. Development of the GC-MS organic aerosol monitor (GC-MS OAM) for in-field detection of particulate organic compounds. *Atmos. Environ.* 169, 258–266.

Dallmann, T.R., Onasch, T.B., Kirchstetter, T.W., et al., 2014. Characterization of particulate matter emissions from on-road gasoline and diesel vehicles using a soot particle aerosol mass spectrometer. *Atmos. Chem. Phys.* 14, 7585–7599.

Deshmukh, D.K., Deb, M.K., Suzuki, Y., et al., 2013. Water-soluble ionic composition of $PM_{2.5-10}$ and $PM_{2.5}$ aerosols in the lower troposphere of an industrial city Raipur, the eastern central India. *Air Qual. Atmos. Health* 6, 95–110.

dos Santos Souza, E.J., Zapata Mora, C., Aristizábal Zuluaga, B.H., et al., 2021. Multi-elemental analysis of particulate matter $PM_{2.5}$ and PM_{10} by ICP OES. *Talanta* 221, 121457.

Drosatou, A.D., Skyllakou, K., Theodoritsi, G.N., et al., 2019. Positive matrix factorization of organic aerosol: insights from a chemical transport model. *Atmos. Chem. Phys.* 19, 973–986.

Engelbrecht, J.P., Menéndez, I., Derbyshire, E., 2014. Sources of $PM_{2.5}$ impacting on Gran Canaria, Spain. *CATENA* 117, 119–132.

European Standards, 2014. Ambient air - Standard gravimetric measurement method for the determination of the PM_{10} or $PM_{2.5}$ mass concentration of suspended particulate matter. https://www.en-standard.eu/csn-en-12341-ambient-air-standard-gravimetric-measurement-method-for-the-determination-of-the-pm10-or-pm2-5-mass-concentration-of-suspended-particulate-matter/ (accessed 10.14.21).

Fang, Y., Chen, Y., Huang, G., et al., 2021. Particulate and Dissolved Black Carbon in Coastal China Seas: Spatiotemporal Variations, Dynamics, and Potential Implications. *Environ. Sci. Technol.* 55, 788–796.

Fang, Y., Naik, V., Horowitz, L.W., et al., 2013. Air pollution and associated human mortality: the role of air pollutant emissions, climate change and methane concentration increases from the preindustrial period to present. *Atmos. Chem. Phys.* 13, 1377–1394.

Feng, J., Chan, C.K., Fang, M., et al., 2006. Characteristics of organic matter in $PM_{2.5}$ in Shanghai. *Chemosphere* 64, 1393–1400.

Feng, J., Li, M., Zhang, P., et al., 2013. Investigation of the sources and seasonal variations of secondary organic aerosols in $PM_{2.5}$ in Shanghai with organic tracers. *Atmos. Environ.* 79, 614–622.

Feng, J., Zhong, M., Xu, B., et al., 2014. Concentrations, seasonal and diurnal variations of black carbon in $PM_{2.5}$ in Shanghai, China. *Atmos. Res.* 147–148, 1–9.

Feng, S., Gao, D., Liao, F., et al., 2016. The health effects of ambient $PM_{2.5}$ and potential mechanisms. Ecotoxicol. Environ. Saf. 128, 67–74.

Feng, T., Du, H., Lin, Z., et al., 2020. Spatial spillover effects of environmental regulations on air pollution: Evidence from urban agglomerations in China. *J. Environ. Manage.* 272, 110998.

Fine, P.M., Cass, G.R., Simoneit, B.R.T., 2004. Chemical Characterization of Fine Particle Emissions from the Wood Stove Combustion of Prevalent United States Tree Species. *Environ. Eng. Sci.* 21, 705–721.

Gao, B., Guo, H., Wang, X.-M., et al., 2013. Tracer-based source apportionment of polycyclic aromatic hydrocarbons in $PM_{2.5}$ in Guangzhou, southern China, using positive matrix factorization (PMF). Environ. *Sci. Pollut. Res.* 20, 2398–2409.

Gao, J., Peng, X., Chen, G., et al., 2016. Insights into the chemical characterization and sources of $PM_{2.5}$ in Beijing at a 1-h time resolution. *Sci. Total Environ.* 542, 162–171.

Gautam, S., Patra, A.K., Kumar, P., 2019. Status and chemical characteristics of ambient $PM_{2.5}$ pollutions in China: a review. Environ Dev Sustain. 21, 1649–1674.

Goldstein, A., Galbally, I., 2007. Known and Unexplored Organic Constituents in the Earth's Atmosphere. *Environ. Sci. Technol.* 41, 1514–1521.

Gonçalves, C., Alves, C., Fernandes, A.P., et al., 2011. Organic compounds in $PM_{2.5}$ emitted from fireplace and woodstove combustion of typical Portuguese wood species. *Atmos. Environ.* 45, 4533–4545.

17

González, L.T., Longoria Rodríguez, F.E., Sánchez-Domínguez, M., et al., 2017. Determination of trace metals in TSP and $PM_{2.5}$ materials collected in the Metropolitan Area of Monterrey, Mexico: A characterization study by XPS, ICP-AES and SEM-EDS. *Atmos. Res.* 196, 8–22.

Gu, Z., Feng, J., Han, W., et al., 2010. Characteristics of organic matter in $PM_{2.5}$ from an e-waste dismantling area in Taizhou, China. *Chemosphere* 80, 800–806.

Guo, H., Ding, A.J., So, K.L., et al., 2009. Receptor modeling of source apportionment of Hong Kong aerosols and the implication of urban and regional contribution. *Atmos. Environ.* 43, 1159–1169.

Gupta, S., Gadi, R., Sharma, S.K., et al., 2018. Characterization and source apportionment of organic compounds in PM_{10} using PCA and PMF at a traffic hotspot of Delhi. *Sustain. Cities Soc.* 39, 52–67.

Gupta, S., Soni, P., Gupta, A.K., 2021. Optimization of WD-XRF analytical technique to measure elemental abundance in $PM_{2.5}$ dust collected on quartz-fibre filter. *Atmos. Pollut. Res.* 12, 345–351.

Hama, S., Kumar, P., Alam, M.S., et al., 2021. Chemical source profiles of fine particles for five different sources in Delhi. *Chemosphere* 274, 129913.

Han, B., Kong, S., Bai, Z., et al., 2010. Characterization of Elemental Species in $PM_{2.5}$ Samples Collected in Four Cities of Northeast China. *Water. Air. Soil Pollut.* 209, 15–28.

Hand, J.L., Schichtel, B.A., Malm, W.C., et al., 2013. Spatial and Temporal Trends in $PM_{2.5}$ Organic and Elemental Carbon across the United States. *Adv. Meteorol.* 2013, e367674.

He, J., Gong, S., Zhou, C., et al., 2018. Analyses of winter circulation types and their impacts on haze pollution in Beijing. *Atmos. Environ.* 192, 94–103.

He, M., Zeng, X., Zhang, K., et al., 2017. Fine Particulate Matter Concentrations in Urban Chinese Cities, 2005–2016: A Systematic Review. *Int. J. Environ. Res. Public Health* 14, 191.

He, K., Yang, F., Duan, F., et al., 2011. Atmospheric Particulate Matter and Regional Compound Pollution. *Science Press*, Beijing, China.

He, L.-Y., Hu, M., Huang, X.-F., et al., 2006. Seasonal pollution characteristics of organic compounds in atmospheric fine particles in Beijing. *Sci. Total Environ.* 359, 167–176.

Hellén, H., Hakola, H., Laurila, T., 2003. Determination of source contributions of NMHCs in Helsinki (60°N, 25°E) using chemical mass balance and the Unmix multivariate receptor models. *Atmos. Environ.* 37, 1413–1424.

Hennigan, C.J., Mucci, A., Reed, B.E., 2019. Trends in $PM_{2.5}$ transition metals in urban areas across the United States. *Environ. Res. Lett.* 14, 104006.

Henry, R.C., 2003. Multivariate receptor modeling by N-dimensional edge detection. *Chemom. Intell. Lab. Syst.* 65, 179–189.

Herrera Murillo, J., Campos Ramos, A., Ángeles García, F., et al., 2012. Chemical composition of $PM_{2.5}$ particles in Salamanca, Guanajuato Mexico: Source apportionment with receptor models. *Atmos. Res.* 107, 31–41.

Ho, K.F., Cao, J.J., Lee, S.C., et al., 2006. Source apportionment of $PM_{2.5}$ in urban area of Hong Kong. *J. Hazard. Mater.* 138, 73–85.

Hopke, P.K., 2016. Review of receptor modeling methods for source apportionment. *J. Air Waste Manag. Assoc.* 66, 237–259.

Hu, D., Bian, Q., Lau, A.K.H., et al., 2010. Source apportioning of primary and secondary organic carbon in summer $PM_{2.5}$ in Hong Kong using positive matrix factorization of secondary and primary organic tracer data. *J. Geophys. Res. Atmos.* 115, D16204.

Hu, G., Zhang, Y., Sun, J., et al., 2014a. Variability, formation and acidity of water-soluble ions in $PM_{2.5}$ in Beijing based on the semi-continuous observations. *Atmos. Res.* 145–146, 1–11.

Hu, S., McDonald, R., Martuzevicius, D., et al., 2006. UNMIX modeling of ambient $PM_{2.5}$ near an interstate highway in Cincinnati, OH, USA. *Atmos. Environ.* 40, 378–395.

Hu, Y., Balachandran, S., Pachon, J.E., et al., 2014b. Fine particulate matter source apportionment using a hybrid chemical transport and receptor model approach. *Atmos. Chem. Phys.* 14, 5415–5431.

Huang, H.-H., Wang, Y.-Q., Li, S.-P., et al., 2020a. Seasonal Variation of Water-soluble Ions in $PM_{2.5}$ in Xi'an. *Huanjing Kexue* 41, 2528–2535.

Huang, L., Zhu, Y., Wang, Q., et al., 2021a. Assessment of the effects of straw burning bans in China: Emissions, air quality, and health impacts. *Sci. Total Environ.* 789, 147935.

Huang, X., Liu, Z., Liu, J., et al., 2017. Chemical characterization and source identification of PM2.5 at multiple sites

in the Beijing–Tianjin–Hebei region, China. *Atmos. Chem. Phys.* 17, 12941–12962.

Huang, X., Tang, G., Zhang, Junke, et al., 2021b. Characteristics of PM2.5 pollution in Beijing after the improvement of air quality. *J. Environ. Sci.* 100, 1–10.

Huang, X.H.H., Bian, Q.J., Louie, P.K.K., et al., 2014. Contributions of vehicular carbonaceous aerosols to $PM_{2.5}$ in a roadside environment in Hong Kong. *Atmos. Chem. Phys.* 14, 9279–9293.

Huang, Y., Lei, C., Liu, C.-H., et al., 2021c. A review of strategies for mitigating roadside air pollution in urban street canyons. *Environ. Pollut.* 280, 116971.

Huang, Y., Surawski, N.C., Yam, Y.-S., et al., 2020b. Re-evaluating effectiveness of vehicle emission control programmes targeting high-emitters. *Nat. Sustain.* 3, 904–907.

Huang, Y., Lee, C.K.C., Yam, Y.S., et al., 2022a. Rapid detection of high-emitting vehicles by on-road remote sensing technology improves urban air quality. *Sci. Adv.* 8, eabl7575.

Huang Y., Ng E.C.Y., Surawski N.C., et al., 2022b. Effect of diesel particulate filter regeneration on fuel consumption and emissions performance under real-driving conditions. *Fuel* 320, 123937.

Ikemori, F., Nishimura, R., Saito, S., et al., 2021. Organic Molecular Tracers in $PM_{2.5}$ at Urban Sites during Spring and Summer in Japan: Impact of Secondary Organic Aerosols on Water-Soluble Organic Carbon. *Atmosphere* 12, 579.

Jain, S., Sharma, S.K., Mandal, T.K., et al., 2018. Source apportionment of PM_{10} in Delhi, India using PCA/APCS, UNMIX and PMF. P*articuology* 37, 107–118.

Ji, D., Cui, Y., Li, L., et al., 2018. Characterization and source identification of fine particulate matter in urban Beijing during the 2015 Spring Festival. *Sci. Total Environ.* 628–629, 430–440.

Karakas, F., Imamoglu, I., Gedik, K., 2017. Positive Matrix Factorization dynamics in fingerprinting: A comparative study of PMF2 and EPA-PMF3 for source apportionment of sediment polychlorinated biphenyls. *Environ. Pollut.* 220, 20–28.

Kong, S., Han, B., Bai, Z., et al., 2010. Receptor modeling of $PM_{2.5}$, PM_{10} and TSP in different seasons and long-range transport analysis at a coastal site of Tianjin, China. *Sci. Total Environ.* 408, 4681–4694.

Lage, J., Wolterbeek, H.T., Reis, M.A., et al., 2016. Source apportionment by positive matrix factorization on elemental concentration obtained in PM_{10} and biomonitors collected in the vicinities of a steelworks. *J. Radioanal. Nucl. Chem.* 309, 397–404.

Lang, J., Zhang, Y., Zhou, Y., et al., 2017. Trends of PM2.5 and Chemical Composition in Beijing, 2000-2015. Aerosol Air Qual. Res. 17, 412–425.

Li, D., Du, Q., Dong, H., et al., 2020. Field measurements on the generation and emission characteristics of $PM_{2.5}$ from industrial fluidized bed boilers. *Energ. Source. Part A* 42(6), 773-784.

Li, L., Lai, W., Pu, J., et al., 2018. Polar organic tracers in $PM_{2.5}$ aerosols from an inland background area in Southwest China: Correlations between secondary organic aerosol tracers and source apportionment. *J. Environ. Sci.* 69, 281–293.

Li, X., Guo, X., Liu, X., et al., 2009. Distribution and sources of solvent extractable organic compounds in $PM_{2.5}$ during 2007 Chinese Spring Festival in Beijing. *J. Environ. Sci.* 21, 142–149.

Li, Y., Cao, J., Li, J., et al., 2013. Molecular distribution and seasonal variation of hydrocarbons in PM2.5 from Beijing during 2006. *Particuology* 11, 78–85.

Liu, W., Xu, Y., Liu, W., et al., 2018. Oxidative potential of ambient PM2.5 in the coastal cities of the Bohai Sea, northern China: Seasonal variation and source apportionment. *Environ. Pollut.* 236, 514–528.

Liu, X., Zhu, J., Van Espen, P., et al., 2005. Single particle characterization of spring and summer aerosols in Beijing: Formation of composite sulfate of calcium and potassium. *Atmos. Environ.* 39, 6909–6918.

Liu, Z., Xie, Y., Hu, B., et al., 2017. Size-resolved aerosol water-soluble ions during the summer and winter seasons in Beijing: Formation mechanisms of secondary inorganic aerosols. *Chemosphere* 183, 119–131.

Lu, S., Liu, D., Zhang, W., et al., 2015. Physico-chemical characterization of PM2.5 in the microenvironment of Shanghai subway. *Atmos. Res.* 153, 543–552.

Lv, B., Zhang, B., Bai, Y., 2016. A systematic analysis of PM2.5 in Beijing and its sources from 2000 to 2012. *Atmos. Environ.* 124, 98–108.

Lyu, R., Shi, Z., Alam, M.S., et al., 2019. Insight into the composition of organic compounds ($\geq$ C_6) in $PM_{2.5}$

in wintertime in Beijing, China. *Atmos. Chem. Phys.* 19, 10865–10881.

Manousakas M., Diapouli E., Belis C.A., et al., 2021. Quantitative assessment of the variability in chemical profiles from source apportionment analysis of PM_{10} and $PM_{2.5}$ at different sites within a large metropolitan area. *Environ. Res.* 192, 110257.

Manousakas, M., Papaefthymiou, H., Eleftheriadis, K., et al., 2014. Determination of water-soluble and insoluble elements in $PM_{2.5}$ by ICP-MS. *Sci. Total Environ.* 493, 694–700.

Mazaheri, M., Bostrom, T.E., Johnson, G.R., et al., 2013. Composition and Morphology of Particle Emissions from in-use Aircraft during Takeoff and Landing. *Environ. Sci. Technol.* 47, 5235–5242.

Miller, M.S., Friedlander, S.K., Hidy, G.M., 1972. A chemical element balance for the Pasadena aerosol. *J. Colloid Interface Sci.* 39, 165–176.

Molino, A., Chianese, S., Musmarra, D., 2016. Biomass gasification technology: the state of the art overview. *J. Energy Chem.* 25, 10–25.

Negral, L., Moreno-Grau, S., Moreno, J., et al., 2008. Natural and Anthropogenic Contributions to PM_{10} and $PM_{2.5}$ in an Urban Area in the Western Mediterranean Coast. *Water. Air. Soil Pollut.* 192, 227–238.

Onat, B., Stakeeva, B., 2013. Personal exposure of commuters in public transport to $PM_{2.5}$ and fine particle counts. *Atmos. Pollut. Res.* 4, 329–335.

Paatero, P., Hopke, P.K., 2003. Discarding or downweighting high-noise variables in factor analytic models. *Anal. Chim. Acta* 490, 277–289.

Paatero, P., Tapper, U., 1993. Analysis of different modes of factor analysis as least squares fit problems. Chemom. *Intell. Lab. Syst.* 18, 183–194.

Park, J., Lee, K.-H., Kim, H., et al., 2021. The impact of organic extracts of seasonal $PM_{2.5}$ on primary human lung epithelial cells and their chemical characterization. *Environ. Sci. Pollut. Res.* 28, 59868-59880.

Perez, L., Tobías, A., Querol, X., et al., 2012. Saharan dust, particulate matter and cause-specific mortality: A case–crossover study in Barcelona (Spain). *Environ. Int.* 48, 150–155.

Pernigotti, D., Belis, C.A., Spanò, L., 2016. SPECIEUROPE: The European data base for PM source profiles. *Atmos. Pollut. Res.* 7, 307–314.

Petrova-Antonova, D., Jelyazkov, J., Pavlova, I., 2021. Air quality monitoring platform with multiple data source support. *Energ. Source. Part A*, article in press.

Polezer, G., Godoi, R.H.M., Potgieter-Vermaak, S., et al., 2020. Atomic Absorption Spectrometry Methods to Access the Metal Solubility of Aerosols in Artificial Lung Fluid. *Appl. Spectrosc.* 74, 932–939.

Popovicheva, O.B., Engling, G., Ku, I.-T., et al., 2019. Aerosol Emissions from Long-lasting Smoldering of Boreal Peatlands: Chemical Composition, Markers, and Microstructure. *Aerosol Air Qual. Res.* 19, 484–503.

Pui, D.Y.H., Chen, S.-C., Zuo, Z., 2014. $PM_{2.5}$ in China: Measurements, sources, visibility and health effects, and mitigation. *Particuology* 13, 1–26.

Samy, S., Hays, M.D., 2013. Quantitative LC–MS for water-soluble heterocyclic amines in fine aerosols ($PM_{2.5}$) at Duke Forest, USA. *Atmos. Environ.* 72, 77–80.

Schauer, J.J., Kleeman, M.J., Cass, G.R., et al., 2002. Measurement of Emissions from Air Pollution Sources. 5. C1−C32 Organic Compounds from Gasoline-Powered Motor Vehicles. *Environ. Sci. Technol.* 36, 1169–1180.

Shaltout, A.A., Boman, J., Welz, B., et al., 2014. Method development for the determination of Cd, Cu, Ni and Pb in $PM_{2.5}$ particles sampled in industrial and urban areas of Greater Cairo, Egypt, using high-resolution continuum source graphite furnace atomic absorption spectrometry. *Microchem. J.* 113, 4–9.

Shaltout, A.A., Hassan, S.K., Karydas, A.G., et al., 2018. Comparative elemental analysis of fine particulate matter ($PM_{2.5}$) from industrial and residential areas in Greater Cairo-Egypt by means of a multi-secondary target energy dispersive X-ray fluorescence spectrometer. *Spectrochim. Acta Part B* 145, 29–35.

Simon, H., Beck, L., Bhave, P.V., et al., 2010. The development and uses of EPA's SPECIATE database. *Atmos. Pollut. Res.* 1, 196–206.

Song, S., Wu, Y., Zheng, X., et al., 2014. Chemical characterization of roadside $PM_{2.5}$ and black carbon in Macao during a summer campaign. *Atmos. Pollut. Res.* 5, 381–387.

Song, Y., Tang, X., Xie, S., et al., 2007. Source apportionment of $PM_{2.5}$ in Beijing in 2004. *J. Hazard. Mater.* 146, 124–130.

Song, Y., Xie, S., Zhang, Y., et al., 2006a. Source apportionment of $PM_{2.5}$ in Beijing using principal component

analysis/absolute principal component scores and UNMIX. *Sci. Total Environ.* 372, 278–286.

Song, Y., Zhang, Y., Xie, S., et al., 2006b. Source apportionment of $PM_{2.5}$ in Beijing by positive matrix factorization. *Atmos. Environ.* 40, 1526–1537.

Sosa, B.S., Porta, A., Colman Lerner, J.E., et al., 2017. Human health risk due to variations in PM_{10}-$PM_{2.5}$ and associated PAHs levels. *Atmos. Environ.* 160, 27–35.

Souza, D.Z., Vasconcellos, P.C., Lee, H., et al., 2014. Composition of $PM_{2.5}$ and PM_{10} Collected at Urban Sites in Brazil. *Aerosol Air Qual. Res.* 14, 168–176.

Tao, J., Zhang, L., Cao, J., et al., 2017. A review of current knowledge concerning $PM_{2.5}$ chemical composition, aerosol optical properties and their relationships across China. *Atmos. Chem. Phys.* 17, 9485–9518.

Tian, P., Wang, G., Zhang, R., et al., 2015. Impacts of aerosol chemical compositions on optical properties in urban Beijing, China. *Particuology* 18, 155–164.

Tian, Y., Liu, X., Huo, R., et al., 2021. Organic compound source profiles of $PM_{2.5}$ from traffic emissions, coal combustion, industrial processes and dust. *Chemosphere* 278, 130429.

Timko, M.T., Albo, S.E., Onasch, T.B., et al., 2014. Composition and Sources of the Organic Particle Emissions from Aircraft Engines. *Aerosol Sci. Technol.* 48, 61–73.

Turap, Y., Talifu, D., Wang, X., et al., 2018. Concentration characteristics, source apportionment, and oxidative damage of $PM_{2.5}$-bound PAHs in petrochemical region in Xinjiang, NW China. *Environ. Sci. Pollut. Res.* 25, 22629–22640.

U.S. Environmental Protection Agency, 1999. 40 CFR Appendix L to Part 50 - Reference Method for the Determination of Fine Particulate Matter as $PM_{2.5}$ in the Atmosphere. https://www.law.cornell.edu/cfr/text/40/appendix-L_to_part_50 (accessed 10.14.21).

U.S. Environmental Protection Agency, 2015a. Positive Matrix Factorization Model for environmental data analyses. https://www.epa.gov/air-research/positive-matrix-factorization-model-environmental-data-analyses (accessed 8.5.21).

U.S. Environmental Protection Agency, 2015b. SPECIATE. https://www.epa.gov/air-emissions-modeling/speciate (accessed 8.6.21).

U.S. Environmental Protection Agency, 2015c. Unmix 6.0 Model for environmental data analyses. https://www.epa.gov/air-research/unmix-60-model-environmental-data-analyses (accessed 8.6.21).

Viana, M., Querol, X., Alastuey, A., et al., 2006. Identification of PM sources by principal component analysis (PCA) coupled with wind direction data. *Chemosphere* 65, 2411–2418.

Voutsa, D., Samara, C., Manoli, E., et al., 2014. Ionic composition of $PM_{2.5}$ at urban sites of northern Greece: secondary inorganic aerosol formation. *Environ. Sci. Pollut. Res.* 21, 4995–5006.

Waheed, S., Jaafar, M.Z., Siddique, N., et al., 2012. PIXE analysis of $PM_{2.5}$ and $PM_{2.5–10}$ for air quality assessment of Islamabad, Pakistan: Application of chemometrics for source identification. *J. Environ. Sci. Health Part A* 47, 2016–2027.

Wang, B., Lee, S.C., Ho, K.F., 2006. Chemical composition of fine particles from incense burning in a large environmental chamber. *Atmos. Environ.* 40, 7858–7868.

Wang, H., Tian, M., Li, X., et al., 2015a. Chemical Composition and Light Extinction Contribution of $PM_{2.5}$ in Urban Beijing for a 1-Year Period. *Aerosol Air Qual. Res.* 15, 2200–2211.

Wang, H., Zhou, Y., Zhuang, Y., et al., 2009a. Characterization of $PM_{2.5}$ /$PM_{2.5-10}$ and source tracking in the juncture belt between urban and rural areas of Beijing. *Chin. Sci. Bull.* 54, 2506–2515.

Wang, H., Zhuang, Y., Wang, Y., et al., 2008. Long-term monitoring and source apportionment of $PM_{2.5}$/PM_{10} in Beijing, China. *J. Environ. Sci.* 20, 1323–1327.

Wang, J., Geng, N.B., Xu, Y.F., et al., 2014a. PAHs in $PM_{2.5}$ in Zhengzhou: concentration, carcinogenic risk analysis, and source apportionment. *Environ. Monit. Assess.* 186, 7461–7473.

Wang, Q., Shao, M., Liu, Y., et al., 2007. Impact of biomass burning on urban air quality estimated by organic tracers: Guangzhou and Beijing as cases. *Atmos. Environ.* 41, 8380–8390.

Wang, Q., Shao, M., Zhang, Y., et al., 2009b. Source apportionment of fine organic aerosols in Beijing. *Atmos. Chem. Phys.* 9, 8573–8585.

Wang, Q., Zhang, D., Liu, B., et al., 2015b. Spatial and temporal variations of ambient $PM_{2.5}$ source contributions using positive matrix factorization. *Chin. Environ. Sci.* 35, 2917–2924.

Wang, S., Zhao, M., Xing, J., et al., 2010. Quantifying the Air Pollutants Emission Reduction during the 2008 Olympic

Games in Beijing. *Environ. Sci. Technol.* 44, 2490–2496.

Wang, W., Maenhaut, W., Yang, W., et al., 2014b. One–year aerosol characterization study for PM$_{2.5}$ and PM$_{10}$ in Beijing. *Atmos. Pollut. Res.* 5, 554–562.

Wang, X., Chow, J.C., Kohl, S.D., et al., 2015c. Characterization of PM$_{2.5}$ and PM$_{10}$ fugitive dust source profiles in the Athabasca Oil Sands Region. *J. Air Waste Manag. Assoc.* 65, 1421–1433.

Wang, X., Zhang, R., Yu, W., 2019. The Effects of PM$_{2.5}$ Concentrations and Relative Humidity on Atmospheric Visibility in Beijing. *J. Geophys. Res. Atmos.* 124, 2235–2259.

Wang, Y., Zhang, Y., Li, X., et al., 2021. Refined Source Apportionment of Atmospheric PM$_{2.5}$ in a Typical City in Northwest China. *Aerosol Air Qual. Res.* 21, 200146.

Wang, Y., Zhuang, G., Tang, A., et al., 2005. The ion chemistry and the source of PM$_{2.5}$ aerosol in Beijing. *Atmos. Environ.* 39, 3771–3784.

Wang, Z., Bi, X., Sheng, G., et al., 2009c. Characterization of organic compounds and molecular tracers from biomass burning smoke in South China I: Broad-leaf trees and shrubs. *Atmos. Environ.* 43, 3096–3102.

Wang, Z., Li, Y., Liu, B., et al., 2016b. Chemical characteristics of PM$_{2.5}$ in Beijing. *Acta Ecol. Sin.* 36, 2382–2392.

Weichenthal, S., Kulka, R., Lavigne, E., et al., 2017. Biomass Burning as a Source of Ambient Fine Particulate Air Pollution and Acute Myocardial Infarction. *Epidemiology* 28, 329–337.

World Health Organization, 2021. Ambient (outdoor) air pollution. https://www.who.int/news-room/fact-sheets/detail/ambient-(outdoor)-air-quality-and-health (accessed 30.03.2022).

Wu, D., Wang, Z., Chen, J., et al., 2014. Polycyclic aromatic hydrocarbons (PAHs) in atmospheric PM$_{2.5}$ and PM$_{10}$ at a coal-based industrial city: Implication for PAH control at industrial agglomeration regions, China. *Atmos. Res.* 149, 217–229.

Wu, X., Cao, F., Haque, M., et al., 2020. Molecular composition and source apportionment of fine organic aerosols in Northeast China. *Atmos. Environ.* 239, 117722.

Xu, H., Ta, W., Yang, L., et al., 2020. Characterizations of PM$_{2.5}$-bound organic compounds and associated potential cancer risks on cooking emissions from dominated types of commercial restaurants in northwestern China. *Chemosphere* 261, 127758.

Xu, J., Ding, G., Yan, P., et al., 2007. Componential Characteristics and Sources Identification of PM$_{2.5}$ in Beijing. *J. Appl. Meteorol. Sci.* 18, 645–654.

Yan, D., Kong, Y., Ye, B., et al., 2021. Spatio-temporal variation and daily prediction of PM$_{2.5}$ concentration in world-class urban agglomerations of China. *Environ. Geochem. Health* 43, 301–316.

Yang, F., He, K., Ye, B., et al., 2005a. One-year record of organic and elemental carbon in fine particles in downtown Beijing and Shanghai. *Atmos. Chem. Phys.* 5, 1449–1457.

Yang, F., Huang, L., Duan, F., et al., 2011. Carbonaceous species in PM$_{2.5}$ at a pair of rural/urban sites in Beijing, 2005–2008. *Atmos. Chem. Phys.* 11, 7893–7903.

Yang, F., Ye, B., He, K., et al., 2005b. Characterization of Atmospheric Mineral Components of PM$_{2.5}$ in Beijing and Shanghai, China. *Sci. Total Environ.* 343, 221–230.

Yang, H., Chen, J., Wen, J., et al., 2016. Composition and sources of PM$_{2.5}$ around the heating periods of 2013 and 2014 in Beijing: Implications for efficient mitigation measures. *Atmos. Environ.* 124, 378–386.

Yang, J., Liu, G., Yao, Y., et al., 2020. Elemental analysis of PM$_{2.5}$ using PIXE and NAA in Xinzhen, Beijing. *J. Radioanal. Nucl. Chem.* 323, 457–463.

Yang, Y., Zhou, R., Wu, J., et al., 2015. Seasonal variations and size distributions of water-soluble ions in atmospheric aerosols in Beijing, 2012. *J. Environ. Sci.* 34, 197–205.

Yao, X., Chan, C.K., Fang, M., et al., 2002. The water-soluble ionic composition of PM$_{2.5}$ in Shanghai and Beijing, China. *Atmos. Environ.* 36, 4223–4234.

Yin, L., Niu, Z., Chen, X., et al., 2014. Characteristics of water-soluble inorganic ions in PM$_{2.5}$ and PM$_{2.5\ 2.5–10}$ in the coastal urban agglomeration along the Western Taiwan Strait Region, China. *Environ. Sci. Pollut. Res.* 21, 5141–5156.

Youn, J.-S., Han, S., Yi, J.-S., et al., 2021. Development of PM$_{10}$ and PM$_{2.5}$ cyclones for small sampling ports at stationary sources: Numerical and experimental study. *Environ. Res.* 193, 110507.

Yu, L., Wang, G., Zhang, R., et al., 2013. Characterization and source apportionment of PM$_{2.5}$ in an urban environment in Beijing. *Aerosol Air Qual. Res.* 13, 574–583.

Yu, Y., Schleicher, N., Norra, S., et al., 2011. Dynamics and origin of PM$_{2.5}$ during a three-year sampling period in

Beijing, China. ***J. Environ. Monit.*** 13, 334–346.

Zhang, L., Wang, C., Zhu, H., et al., 2016. Characterization and source apportionment of PM$_{2.5}$ in mixed function area during summer and winter, Beijing. ***Chin. Environ. Sci.*** 36, 36–41.

Zhang, H., Xing, Y., Cheng, S., et al., 2021a. Characterization of multiple atmospheric pollutants during haze and non-haze episodes in Beijing, China: Concentration, chemical components and transport flux variations. ***Atmos. Environ.*** 246, 118129.

Zhang, K., Yang, L., Li, Q., et al., 2021b. Hourly measurement of PM$_{2.5}$-bound nonpolar organic compounds in Shanghai: Characteristics, sources and health risk assessment. ***Sci. Total Environ.*** 789, 148070.

Zhang, L., Wang, T., Lv, M., et al., 2015. On the severe haze in Beijing during January 2013: Unraveling the effects of meteorological anomalies with WRF-Chem. ***Atmos. Environ.*** 104, 11–21.

Zhang, R., Jing, J., Tao, J., et al., 2013. Chemical characterization and source apportionment of PM$_{2.5}$ in Beijing: seasonal perspective. ***Atmos. Chem. Phys.*** 13, 7053–7074.

Zhang, R., Khalizov, A., Wang, L., et al., 2012. Nucleation and Growth of Nanoparticles in the Atmosphere. ***Chem. Rev.*** 112, 1957–2011.

Zhang, T., Claeys, M., Cachier, H., et al., 2008. Identification and estimation of the biomass burning contribution to Beijing aerosol using levoglucosan as a molecular marker. ***Atmos. Environ.*** 42, 7013–7021.

Zhang, W., Guo, J., Sun, Y., et al., 2007. Source apportionment for urban PM$_{10}$ and PM$_{2.5}$ in the Beijing area. ***Chin. Sci. Bull.*** 52, 608–615.

Zhang, Y., Lang, J., Cheng, S., et al., 2018. Chemical composition and sources of PM$_1$ and PM$_{2.5}$ in Beijing in autumn. ***Sci. Total Environ.*** 630, 72–82.

Zhang, Y., Cai, J., Wang, S., et al., 2017a. Review of receptor-based source apportionment research of fine particulate matter and its challenges in China. ***Sci. Total Environ.*** 586, 917–929.

Zhang, Z., Wang, W., Cheng, M., et al., 2017b. The contribution of residential coal combustion to PM$_{2.5}$ pollution over China's Beijing-Tianjin-Hebei region in winter. ***Atmos. Environ.*** 159, 147–161.

Zhao, P.S., Dong, F., He, D., et al., 2013. Characteristics of concentrations and chemical compositions for PM$_{2.5}$ in the region of Beijing, Tianjin, and Hebei, China. ***Atmos. Chem. Phys.*** 13, 4631–4644.

Zhao, S., Tian, H., Luo, L., et al., 2021. Temporal variation characteristics and source apportionment of metal elements in PM$_{2.5}$ in urban Beijing during 2018–2019. ***Environ. Pollut.*** 268, 115856.

Zhao, X., Zhang, X., Xu, X., et al., 2009. Seasonal and diurnal variations of ambient PM$_{2.5}$ concentration in urban and rural environments in Beijing. ***Atmos. Environ.*** 43, 2893–2900.

Zhao, X., Yan, H., Liu, M., et al., 2018. Relationship between PM$_{2.5}$ adsorption and leaf surface morphology in ten urban tree species in Shenyang, China. ***Energ. Source. Part A*** 41(8), 1029-1039.

Zheng, M., Salmon, L.G., Schauer, J.J., et al., 2005. Seasonal trends in PM$_{2.5}$ source contributions in Beijing, China. ***Atmos. Environ.*** 39, 3967–3976.

Zheng, M., Zhang, Y., Yan, C., et al., 2014. Review of PM$_{2.5}$ Source Apportionment Methods in China. ***Acta Sci. Nat. Univ. Pekin.*** 50, 1141–1154.

Zhou, J., Xiong, Y., Xing, Z., et al., 2017. Characterizing and sourcing ambient PM$_{2.5}$ over key emission regions in China II: Organic molecular markers and CMB modeling. ***Atmos. Environ.*** 163, 57–64.

Zíková, N., Wang, Y., Yang, F., et al., 2016. On the source contribution to Beijing PM$_{2.5}$ concentrations. ***Atmos. Environ.*** 134, 84–95.