A point-by-point response to the reviews

Thank you for your valuable comments. The followings are our responses to your comments.

Response to Reviewer #1

Comment 1: This manuscript by Liu et al. reports $PM_{2.5}$ and its major components in winter and spring seasons at four sites in North China. Chemical compositions and spatial difference are discussed. The major sources are also attributed. Generally, the study is well-designed and the manuscript should be published after my concerns are addressed.

Answer: Thank you for your positive evaluation of our work. The followings are our responses to your comments.

Comment 2: Line 144-159. The authors claim that Cl/Na ratio is 1.4 in coal combustion. And if the ratio high than 1.4, atmospheric Cl and Na would be considered to be totally from coal combustion. In fact, biomass burning, including wild fires, open straw burning and biofuel combustion also emits Na and Cl with the Cl/Na ratios of 1-6 (e.g. Schauer ES&T 2001). Moreover, the OC/EC ratios in biomass burning samples are as high as those in coal combustion (Table 3). Since biofuel combustion for heating is also enhanced during winter in the northern China, why and how did the authors rule out the influence of biomass burning on $PM_{2.5}$ at the four sites?

Answer: Yes, you are right. Biomass burning is indeed an important source for atmospheric Na^+ and Cl^-, with the Cl^-/Na^+ ratios of 1-6 (Schauer et al., 2001). However, biomass burning in the NCP region is mainly focusing on the harvest seasons in summer and autumn (Zong et al., 2016), and few farmers are currently combusting crop straws for household cooking and heating because of the inconvenience of biomass with respect to coal and liquid gas.

The ratios of OC and EC to K^+ from biomass burning had been measured to be about 3.9 and 0.8, respectively (Li et al., 2007; Yao et al., 2016), which was about one order of magnitude less than those (34.0 ± 9.3 for OC/ K^+ and 6.9 ± 1.7 for EC/ K^+) measured in this study. Assuming the atmospheric K^+ measured in this study was totally from biomass burning, the contribution of biomass burning to atmospheric carbonaceous aerosols could be roughly estimated to be only 2.8%-5.2% in $PM_{2.5}$ based on the typical ratios of OC and EC to K^+ from biomass burning and the mass proportions of K^+ (0.6%-1.1%, Fig. 11). Therefore, biomass burning during the sampling period in this study made minor contribution to atmospheric $PM_{2.5}$. According to your pertinent comment, the corresponding paragraph has been rephrased in the revised manuscript.

Comment 3: The authors discuss the spatial difference of $PM_{2.5}$ and the major components at the four sites. Did the meteorological conditions, such as planetary boundary layer (PBL), cause such a spatial difference?

Answer: The meteorological conditions, especially wind speed and planetary boundary layer (PBL), play pivotal roles in the dispersion and accumulation of atmospheric pollutants, which can cause spatial and temporal difference of pollutants. As for the sampling sites of BD, WD and DBT, the meteorological conditions could be considered as the same because of the short distances (< 36 km) among them, and hence the spatial difference of $PM_{2.5}$ and the major components at the three sampling sites was rationally ascribed to the different source strengths. Although the distance between the sampling sites of BJ and BD is about 156 km, there was no significant difference of the wind speeds between the two sampling sites during the sampling period (1.4 ± 1.4 m/s for BJ and 1.7 ± 1.1 m/s for BD, Fig. 3). Therefore, the spatial difference of $PM_{2.5}$ and the major components between the sampling sites of BJ and the other three could not be ascribed to the difference of the wind speeds. Because the information of PBL was not available in the region of Baoding, it is difficult to discuss the impact of PBL on the spatial difference of the pollutants. According to your pertinent comment, the corresponding paragraph has been rephrased in the revised manuscript.

Comment 4: SOC is estimated by the EC-tracer OC/EC method. However, previous studies have demonstrated that this method could overestimate SOC under the influence of coal combustion and biomass burning, especially in wintertime. As discussed in the manuscript, coal combustion (maybe also biofuel combustion) had significant impact on PM at the sampling sites in wintertime. Thus, the concentrations and mass fractions of SOC in the winter (Figure 11) should be overestimated.

Answer: Yes, we totally agree with your comment. Because the lowest 10 % percentile of OC/EC ratios (3.5) measured during the sampling period were obviously less than that (13.1, Table 3) from residential coal combustion, POC could be underestimated by the product of the lowest OC/EC ratio and EC measured, and SOC could be overestimated through the subtraction of POC from OC. The overestimation of SOC by the EC-tracer OC/EC method has been noted by previous studies (Ding et al., 2012; Cui et al., 2015). The statement has been inserted in the revised manuscript.

Comment 5: The citation need to be re-formatted throughout the main text. For example, in line 48, the citation formats for the two references are different (Huang et al., 2014; P. Liu et al., 2016).

Answer: According to the citation style of the ACP, "Huang et al., 2014" is commonly the standard format. However, "P. Liu et al., 2016", "J. Liu et al., 2016" and "C. Liu et al., 2016" are often used to distinguish the references that first authors are different but both the last names of first authors and the publication years of the papers are the same.

Comment 6: Line 230-232. Is the difference in concentrations statistically significant? Please add p-value to show the significance of the observed difference.

Answer: Yes. The one-way ANOVA analysis results of the concentrations of OC, EC, NH_4^+, NO_3^-, SO_4^{2-}, Cl^- and K^+ at the four sampling sites are list in Table R1. The statistically significant differences among them were found with the p-values all lower than 0.01. The p-value ($p < 0.01$) has been added in our revised manuscript.

Table R1. The one-way ANOVA analysis for the concentrations of OC, EC, NH_4^+, NO_3^-, SO_4^{2-}, Cl^- and K^+ at the four sampling sites.

		Sum of Squares	df	Mean Square	F	Sig.
OC	Between Groups	56870.407	3	18956.802	19.096	.000
	Within Groups	76439.111	77	992.716		

	Total	133309.519	80			
EC	Between Groups	3036.393	3	1012.131	18.014	.000
	Within Groups	4326.303	77	56.186		
	Total	7362.696	80			
NH_4^+	Between Groups	2029.908	3	676.636	7.820	.000
	Within Groups	6662.556	77	86.527		
	Total	8692.465	80			
NO_3^-	Between Groups	1254.055	3	418.018	4.188	.008
	Within Groups	7685.732	77	99.815		
	Total	8939.787	80			
SO_4^{2-}	Between Groups	2003.050	3	667.683	4.205	.008
	Within Groups	12227.563	77	158.800		
	Total	14230.613	80			
Cl^-	Between Groups	934.896	3	311.632	14.889	.000
	Within Groups	1611.608	77	20.930		
	Total	2546.503	80			
K^+	Between Groups	73.109	3	24.370	19.524	.000
	Within Groups	96.109	77	1.248		
	Total	169.218	80			

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Response to Reviewer #2

Comment 1: The air pollution is very serious in China especially the North China during winter.

Moreover, the rapid formation of $PM_{2.5}$ is more frequency, and the reason of this phenomenon is not very clearly. This article studied the concentration, composition, and the correlations of the key species of $PM_{2.5}$ in four sampling sites of North China. The study demonstrated that the residential coal combustion was dominant source of atmospheric OC, EC, Cl^-, NO_3^-, SO_4^{2-} and NH_4^+ in both rural areas and cities in the four sites of North China. The author also used the CMC method to calculate the contributions of the primary particle emission from residential coal combustion to $PM_{2.5}$ at the four sites during winter. The article is suitable to be published in this Journal. I recommended it to be accepted after minor revision.

Answer: Thank you for your positive evaluation of our work. The followings are our responses to your comments.

Comment 2: line 361: The author demonstrated that the formation rate of SO_4^{2-} via heterogeneous or multiphase reactions might be slower, so the correlation between OC (or EC) and SO_4^{2-} was insignificant. This conclusion is not convinced. The author should give more evidence to support this point, such as some analyzing of trace gases (SO_2, CO, NO_x and so on) during the period in four sites or reference some laboratory studies on the formation rate of SO_4^{2-} via heterogeneous or multiphase reactions.

Answer: Thank you for your valuable suggestion. The reactive uptake coefficients of SO_2 oxidation by O_3 were reported to be from 4.3×10^{-8} to 7×10^{-7} on different mineral aerosols and from 1×10^{-6} to 6×10^{-6} on soot particles (Wu et al., 2011; Song et al., 2012), which were at least one order of magnitude less than those of NO_2 (1.03×10^{-2}-3.43×10^{-3} on soot particles and 1.03×10^{-6}-1.2×10^{-5} on mineral aerosols) (Underwood et al., 2001; Esteve et al., 2004; Ma et al., 2011; Ma et al., 2017). The information has been added in the revised manuscript.

Comment 3: There are some grammar error, the author should improve the English of the article.

Answer: According to your suggestion, the English of the manuscript has been improved through carefully correcting grammar errors, which has been marked in the revised manuscript.

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A list of all relevant changes made in the manuscript

Based on the valuable comments and suggestions of the two reviewers, the followings are a list of all relevant changes made in the manuscript.

1. The discussion about the impact of biomass burning on atmospheric aerosols in winter has been added in our revised manuscript.
2. Solid evidences about the relatively slow formation rate of SO_4^{2-} via heterogeneous or multiple reactions have been added in our revised manuscript.
3. The statement about the overestimation of SOC by EC-tracer OC/EC method has been added in our revised manuscript.
4. The discussion about the influence of meteorological conditions on the spatial difference of $PM_{2.5}$ and the major components has been added in our revised manuscript.
5. The statistically significant difference of the major component concentrations has been analyzed and the p-value has been inserted in our revised manuscript.
6. Some logical and grammatical mistakes have been corrected in our revised manuscript.
7. Several references have been inserted to confirm our points in our revised manuscript.

The contribution of residential coal combustion to atmospheric $PM_{2.5}$ in the North China during winter

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Abstract: The vast area in the North China, especially during wintertime, is currently suffering from severe haze events due to the high levels of atmospheric $PM_{2.5}$. To recognize the reasons for the high levels of $PM_{2.5}$, daily samples of $PM_{2.5}$ were simultaneously collected at the four sampling sites of Beijing City (BJ), Baoding City (BD), Wangdu County (WD) and Dongbaituo Countryside (DBT) during the winters and springs of 2014-2015. The concentrations of the typical water-soluble ions (WSIs, such as Cl^-, NO_3^-, SO_4^{2-} and NH_4^+) at DBT were found to be remarkably higher than those at BJ in the two winters, but almost the same as those at BJ in the two springs. The evidently greater concentrations of OC, EC and secondary inorganic ions (NO_3^-, SO_4^{2-}, NH_4^+ and Cl^-) at DBT than at WD, BD and BJ during the winter of 2015 indicated that the pollutants in the rural area were not due to transportation from its neighbor cities but dominated by local emissions. As the distinct source for atmospheric OC and EC in the rural area, the residential coal combustion also made contribution to secondary inorganic ions through the emissions of their precursors (NO_x, SO_2, NH_3 and HCl) as well as heterogeneous or multiphase reactions on the surface of OC and EC. The average mass proportions of OC, EC, NO_3^- and SO_4^{2-} at BD and WD were found to be very close to those at DBT, but evidently different from those at BJ, implying that the pollutants in the cities of WD and BD which are fully surrounded by the countryside were strongly affected by the residential coal combustion. The OC/EC ratios at the four sampling sites became the almost same value of 4.8 when the concentrations of $PM_{2.5}$ were greater than 150 $\mu g\ m^{-3}$, suggesting that the residential coal combustion could also make dominant contribution to atmospheric $PM_{2.5}$ at BJ during the severe pollution period when the air parcels were usually from southwest–south regions where high density of farmers reside. The evident increase of the number of the species involved in significant correlations from the countryside to the cities further confirmed that residential coal combustion was preferentially dominant source for the key species in the rural area whereas the complex sources including local emissions and regional transportation were dominant for atmospheric species in the cities. The significant correlations among OC, EC, Cl^-, NO_3^-, and NH_4^+ were found at the four sampling sites but only significant correlation between OC (or EC) and SO_4^{2-} was found at BJ, implying that the formation rate of SO_4^{2-} via heterogeneous or multiphase reactions might be

relatively slower than those of NO_3^-, NH_4^+ and Cl^-. Based on the chemical mass closure (CMC) method, the contributions of the primary particle emission from residential coal combustion to atmospheric $PM_{2.5}$ at BJ, BD, WD and DBT were estimated to be 32 %, 49 %, 43 % and 58 %, respectively.

1 Introduction

In recent years, the vast area in the North China is frequently suffering from severe haze pollution (Chan and Yao, 2008; Zhang et al., 2012; Zhang et al., 2015), which has aroused great attention to the public (Guo et al., 2014; Huang et al., 2014; Cheng et al., 2016; Wang et al., 2016; J. Liu et al., 2016). The severe haze pollution is mainly due to the high level of fine particulate matters with dynamic diameter less than 2.5μm ($PM_{2.5}$) (Huang et al., 2014; P. Liu et al., 2016). $PM_{2.5}$ can reduce atmospheric visibility by absorbing or scattering the incident light (Buseck and Posfai, 1999; Cheng et al., 2006) and increase morbidity and mortality by penetrating the human bronchi and lungs (Nel, 2005; Poschl, 2005; Peplow, 2014).

To alleviate the serious haze pollution problems, the Chinese government has performed a series of control measures for major pollution sources (Zhang et al., 2012; J. Liu et al., 2016; Li et al., 2016b; Wen et al., 2016). For example, coal-fired power plants have been forced to install flue gas desulfurization and denitration (Zhang et al., 2012; Chen et al., 2014), coal has been replaced with natural gas and electricity in megacities (Wang et al., 2009; Duan et al., 2012; Zhao et al., 2013a; Tan et al., 2016), stricter emission standards have been implemented for vehicles and industrial boilers (Zhang et al., 2012; Tang et al., 2016) and so on, resulting in the decrease trend of primary pollutants including $PM_{2.5}$ in recent years (Ma et al., 2016; Wen et al., 2016; Zhang et al., 2016). However, the $PM_{2.5}$ levels still achieved to be above 1000 μg m^{-3} in some areas of Beijing-Tianjin-Hebei (BTH) region during the period of the red alert for haze in December 2016 (http://english.mep.gov.cn/News_service/media_news/201612/t20161220_369317.shtml) when the stricter control measures (e.g. stop production for industries and construction, and the odd and even number rule) had been performed (Y. Li et al., 2016), implying that sources other than industries, construction and vehicles might make dominant contribution to atmospheric $PM_{2.5}$ in the region. Residential coal combustion which is prevailing for heating during winter in the region was suspected to be a dominant source for atmospheric $PM_{2.5}$. Although annual residential coal consumption (about 4,200,000 kg) in BTH region only accounts for small fraction (about 11 %) of the total coal consumption (http://www.qstheory.cn/st/dfst/201306/t20130607_238302.htm), the emission factors of primary pollutants including $PM_{2.5}$ from the residential coal combustion have been found to be about 1-3 orders of magnitude greater than those from coal combustion of industries and power plants (Revuelta et al., 1999; Chen et al., 2005; Xu et al., 2006; Zhang et al., 2008; Geng et al., 2014; Yang et al., 2016). In addition, annual residential coal consumption mainly focuses on the four months in winter. Although the Chinese government has implemented control measures for residential coal combustion (e.g. replacement of traditional coal stoves by new stoves, bituminous coal by anthracite, and coal by electricity and natural gas), the promotion strength of the control measures ~~was~~ is still very limited. Additionally, the promotion new stoves are still with strong smoke emission due to lack of clean combustion technique, and the anthracite is not welcomed by farmers because of its extremely slow combustion rate in comparison with bituminous coal.

There were few studies focusing on the influence of residential coal combustion on atmospheric particles in the North China. W. Li et al. (2014) concluded that strong sources for PM_{10} in rural residential areas were from household solid fuel combustion, based on annual mean PM_{10} concentrations observed in urban regions (180 ± 171 μg m^{-3}) and rural villages (182 ± 154 μg m^{-3})

in the northern China. Duan et al. (2012) inferred that the lower OC/EC ratios at the rural site than at the urban site ~~was~~ were ascribed to coal combustion prevailed in the rural area. Our previous study revealed that residential coal combustion made evident contribution to atmospheric water-soluble ions (WSIs) in Beijing (P. Liu et al., 2016). Based on Weather Research and Forecasting model coupled with Chemistry, J. Liu et al. (2016) recently estimated that the residential sources (solid fuel) contributed 32 % and 53 % of the primary $PM_{2.5}$ emissions in the BTH region during the whole year and during the winter of 2010, respectively.

In this study, daily samples of $PM_{2.5}$ were simultaneously collected at the four sampling sites (Beijing City, Baoding City, Wangdu County and Dongbaituo Countryside) during the winters and springs of 2014-2015, and the direct evidence for the influence of residential coal combustion on regional $PM_{2.5}$ in the region was found based on the $PM_{2.5}$ levels, the $PM_{2.5}$ composition characteristics, the correlations among the key species in $PM_{2.5}$, the back trajectories and the chemical mass closure method.

2 Materials and methods

2.1 Sampling sites

The two sampling sites in Beijing City and Dongbaituo Countryside, which have been described in detail by our previous study (P. Liu et al., 2016), were selected on a rooftop (approximately 25 m and 5 m above ground, respectively) of the Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences (RCEES, CAS) and a field station in the agricultural field of Dongbaituo village, Baoding, Hebei Province, respectively. Another two sampling sites in Baoding City and Wangdu County were both chosen on the rooftop of local environmental monitor station (about 30 m and 20 m above ground, respectively), which are both located in the center of the cities and surrounded by some commercial and residential areas. The spatial ~~detailed~~ locations of the four sampling sites ~~is~~ are presented in Fig. 1 and the distances between Beijing and Baoding, Baoding and Wangdu, Wangdu and Dongbaituo are about 156 km, 36 km and 12 km, respectively. Thereafter, the sampling sites of Beijing, Baoding, Wangdu and Dongbaituo are abbreviated as BJ, BD, WD and DBT, respectively.

2.2 Sample collection and analysis

$PM_{2.5}$ samples at BJ and DBT were collected simultaneously on PTFE filters (90 mm, Millipore) by medium-volume $PM_{2.5}$ samplers (LaoYing-2034) at a flow rate of 100 L min^{-1} from January 15, 2014 to May 31, 2015, in winter (January 15, 2014-Febrary 25, 2014, November 18, 2014-January 20, 2015 and February 11, 2015-March 15, 2015) and spring (April 21, 2014-May 4, 2014 and March 20, 2015-May 31, 2015). An enhanced observation at BJ, BD, WD and DBT ~~which added the other two sampling sites of BD and WD~~ was carried out from January 21 to February 10, 2015 and $PM_{2.5}$ samples ~~at the four sampling sites~~ were collected in the same way on the quartz fiber filters (90 mm, Munktell) ~~from January 21 to February 10, 2015~~. The sampling duration was 24 h (from 15:00 p.m. to 15:00 p.m. of the following day in local time (UTC + 8)). All the samples were put in the appropriative dishes (90 mm, Millipore) after sampling and preserved in a refrigerator immediately until analysis.

As for the quartz fiber filters, half of each filter was extracted ultrasonically with 10 mL ultrapure water for half an hour. The solutions were filtered through a micro-porous membrane (pore size, 0.45 μm; diameter, 13 mm) before analysis and the WSIs (Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, Mg^{2+}, Ca^{2+} and K^+) in the treated filtrates were analyzed by Ion Chromatography (IC, WAYEE IC6200) which has been described in detail by our previous study (P. Liu et al., 2016). A quarter of each filter was cut into fragments and digested with 5 mL 65 % HNO_3 and 2 mL 30 % H_2O_2 (Li et al., 2015) by a microwave digestion system (SINEO, MASTER-40). The digestion solution was diluted to 25 mL with ultrapure water to insure the solution acidity below 10 % and the trace elements (Al, Mn, Fe, Cu, Zn, As, Se, Sr, Tl and Pb) in the diluted solution were analyzed by a triple-quadrupole inductively coupled plasma mass spectrometry (ICP-MS/MS, Agilent 8800). The standard reference material (GBW07427) was also digested ~~in~~ as the same way as the samples and the recoveries of the trace elements were within the allowable ranges of the certified values (100 ± 15 %). Another quarter of each filter was analyzed by a DRI thermal optical carbon analyzer (DRI-2001A) for carbon components (OC and EC). In addition, the PTFE filters were only used for analyzing the WSIs (P. Liu et al., 2016).

2.3 Chemical mass closure

Chemical mass closure (CMC) method was adopted by considering secondary inorganic aerosols (SIA, the sum of SO_4^{2-}, NO_3^- and NH_4^+), sea salt & coal combustion (derived from Cl^- and Na^+), biomass burning (characterized by K^+), mineral dust, EC, primary organic carbon (POC), secondary organic carbon (SOC) and trace element oxide (TEO) (Hsu et al., 2010b; Zhang et al., 2013; Mantas et al., 2014; Tian et al., 2014; Kong et al., 2015).

Atmospheric Na^+ and Cl^- were considered to be from ~~both~~ sea salt (Brewer, 1975; van Eyk et al., 2011), ~~and~~ coal combustion (Bläsing and Müller, 2012; Yu et al., 2013; Wu et al., 2014; He et al., 2015; P. Liu et al., 2016) and biomass burning (Zong et al., 2016; Yao et al., 2016) ~~during winter in the North China (Brewer, 1975; van Eyk et al., 2011; Bläsing and Müller, 2012; Yu et al., 2013; Wu et al., 2014; He et al., 2015; P. Liu et al., 2016), and their mass concentrations followed the four equations:~~. However, biomass burning in the NCP region is mainly focusing on the harvest seasons in summer and autumn (Zong et al., 2016), and few farmers are currently combusting crop straws for household cooking and heating because of the inconvenience of biomass with respect to coal and liquid gas. Thus, only sea salt and coal combustion were considered for the estimation of mass concentrations for atmospheric Na^+ and Cl^- in this study based on the following equations:

$$[Cl^-_{cc}] + [Cl^-_{ss}] = [Cl^-] \tag{1}$$

$$[Na^+_{cc}] + [Na^+_{ss}] = [Na^+] \tag{2}$$

$$\frac{[Cl^-_{cc}]/35.5}{[Na^+_{cc}]/23} = 1.4 \tag{3}$$

$$\frac{[Cl^-_{ss}]/35.5}{[Na^+_{ss}]/23} = 1.18 \tag{4}$$

where $[Cl^-_{ss}]$ and $[Na^+_{ss}]$ are the mass concentrations of Cl^- and Na^+ from sea salt, and $[Cl^-_{cc}]$ and $[Na^+_{cc}]$ are the mass concentrations of Cl^- and Na^+ from coal combustion. The molar ratio of Cl^-_{ss} to Na^+_{ss} was adopted to be 1.18 which represented the typical ratio from sea salt (Brewer, 1975). The molar ratio of Cl^-_{cc} to Na^+_{cc} was chosen to be 1.4 in this study according to our preliminary measurements from the raw bituminous coal prevailed in the North China and the value of 1.4 has been recorded by the previous study (Bläsing and Müller, 2012). If the molar ratios of atmospheric Cl^- to Na^+ in $PM_{2.5}$ were greater than the value of 1.4 or lower than the value of 1.18, atmospheric Cl^- and Na^+ would be considered to be totally from coal combustion or sea salt.

Because the average Al content accounts for about 7 % in mineral dust (Zhang et al., 2003; Ho et al., 2006; Hsu et al., 2010a; Zhang et al., 2013), the mineral dust was estimated based on the follow equation:

$$[Mineral\ dust] = \frac{[Al]}{0.07} \tag{5}$$

POC and SOC were calculated by the EC-tracer OC/EC method (Cheng et al., 2011; Zhao et al., 2013b; G. J. Zheng et al., 2015; Cui et al., 2015) as follows:

$$[POC] = [EC] \times \left({[OC]}/{[EC]}\right)_{pri} = K[EC] + M \tag{6}$$

$$[SOC] = [OC] - [POC] \tag{7}$$

The values of K and M are estimated by linear regression analysis using the data pairs with the lowest 10 % percentile of ambient OC/EC ratios. It should be mentioned that POC could be underestimated and SOC could be overestimated by the EC-tracer OC/EC method, because the lowest 10 % percentile of OC/EC ratios measured were usually less than those from dominant sources of coal combustion and biomass burning in autumn and winter (Ding et al., 2012; Cui et al., 2015).

To estimate the contribution of heavy metal oxide, the enrichment factors (EF) of various heavy metal elements were calculated by the following equation (Hsu et al., 2010b; Zhang et al., 2013):

$$\mathrm{EF} = \frac{\left({[Element]}/{[Al]}\right)_{aerosol}}{\left({[Element]}/{[Al]}\right)_{crust}} \tag{8}$$

where $([\mathrm{Element}]/[\mathrm{Al}])_{\mathrm{aerosol}}$ is the ratio of the element to Al in aerosols and $([\mathrm{Element}]/[\mathrm{Al}])_{\mathrm{crust}}$ is the ratio of the element to Al in the average crust (Taylor, 1964). According to the method developed by Landis et al. (2001), the atmospheric concentrations of elements were multiplied by a factor of 0, 0.5 and 1 if their EFs were less than 1, between 1 and 5, and greater than 5, respectively. Based on the EFs (Fig. 2), the equation for estimating TEO was derived as following:

$$[TEO] = 1.3 \times ([Cu] + [Zn] + [Pb] + [As] + [Se] + [Tl] + 0.5 \times [Mn]) \tag{9}$$

The value of 1.3 was the conversion factor of metal abundance to oxide abundance. It should be mentioned that some other elements such as Cd and Ba were not measured in this study, probably resulting in underestimating the proportion of TEO. Nevertheless, the biases are probably insignificant because the proportion of TEO only accounted for less than 2 % in $PM_{2.5}$.

2.4 Meteorological, trace gases and back trajectory

Both the meteorological data, including wind speed, wind direction, relative humidity (RH), temperature, barometric pressure and air quality index (AQI) of $PM_{2.5}$, SO_2, NO_2, CO, O_3 at BJ, BD and WD were obtained from Beijing urban ecosystem research station in RCEES, CAS (http://www.bjurban.rcees.cas.cn/), environmental protection bureau of Baoding City (http://bdhb.gov.cn/) and environmental monitoring station of Wangdu County (http://www.wdx.gov.cn/), respectively. The meteorological data at BJ and BD ~~is~~ are shown in Fig. 3 and the average concentrations of SO_2 and NO_2 at BJ, BD and WD are listed in Table 2 during the sampling period in the winter of 2015, which ~~would~~ will be discussed in section 3.2 and 3.3. The air mass backward trajectories were calculated for 24 h through the National Oceanic and Atmospheric Administration (NOAA) Hybrid Single-Particle Lagrangian Integrated Trajectory Version 4 model (HYSPLIT 4 model) with National Centers for Environmental Prediction's (NCEP) global data. The backward trajectories arriving at 500 m above sampling position were computed at 0:00 h, 6:00 h, 12:00 h and 18:00 h (UTC) for each sampling day, respectively. A K-means cluster method was then used for classifying the trajectories into several different clusters and suitable clusters were selected for further analysis.

3 Results and discussion

3.1 Comparison of atmospheric WSIs between the two sampling sites of BJ and DBT

The daily variations of atmospheric WSIs during the sampling periods at ~~the two sampling sites of~~ BJ and DBT are shown in Fig. 4. It is evident that the variations of the WSIs between the two sampling sites of BJ and DBT exhibited similar trend, but the mass concentrations of the WSIs were remarkably greater at DBT than at BJ during the two winter seasons. As listed in Table 1, the average concentrations of the typical WSIs were a factor of 1.5-2.0 greater at DBT than at BJ during the two winter seasons, whereas they were approximately the same at the two sampling sites during the two spring seasons. To clearly reveal the differences, the daily D-values (the concentrations of WSIs at DBT minus those at BJ) of several typical WSIs as well as the total WSIs between the two sampling sites of DBT and BJ are individually illustrated in Fig. 5. With only the exception for Ca^{2+} (typical mineral dust component), the D-values of NH_4^+, NO_3^-, SO_4^{2-} and Cl^- between the two sampling sites of DBT and BJ exhibited obviously positive values during the most sampling days in the two winter seasons, implying that the sources related to mineral dust could be excluded for explaining the obviously higher concentrations of the WSIs at DBT than at BJ. The sampling site of DBT is adjacent to Baoding city where the AQI during the winter always ranked the top three among Chinese cities in recent years (http://113.108.142.147:20035/emcpublish/), and hence the relatively greater concentrations of the WSIs at DBT might be due to the regional pollution. However, the emissions of pollutants from industries, power plants and vehicles are usually relatively stable, which could not account for the remarkable differences of the D-values between the winters and the springs (Fig. 5). If the relatively high concentrations of the WSIs at DBT during the winter were ascribed to the regional pollution, there would be additional strong sources for them in the area of Baoding. To explore whether the regional pollution was responsible for the relatively high concentrations of the WSIs at DBT in winter, the various species in $PM_{2.5}$ collected simultaneously at DBT and its neighbor cities of WD, BD and BJ in the winter of 2015 were further investigated in the following section.

3.2 Daily variations of the species in $PM_{2.5}$ at the four sampling sites

The daily variations of the species in $PM_{2.5}$ at the four sampling sites also exhibited similar fluctuation trends (Fig. 6), but there was obvious difference ($p < 0.01$) in the concentrations of OC, EC, NH_4^+, NO_3^-, SO_4^{2-}, Cl^- and K^+ among the four sampling sites, ranked in order as BJ < WD < BD < DBT. The meteorological conditions, especially wind speed and planetary boundary layer (PBL), play pivotal roles in the dispersion and accumulation of atmospheric pollutants ~~implying that the regional meteorological conditions which are dominant factors for the dispersion and accumulation of atmospheric pollutants~~ (Xu et al., 2011; Tao et al., 2012; Sun et al., 2013; Chen et al., 2015; Gao et al., 2016), which can cause spatial and temporal difference of pollutants. As for the sampling sites of BD, WD and DBT, the meteorological conditions could be considered as the same because of the short distances (< 36 km) among them, and hence the spatial difference of $PM_{2.5}$ and the major components at the three sampling sites was rationally ascribed to the different source strengths. Although the distance between the sampling sites of BJ and BD is about 156 km, there was no significant difference of the wind speeds between the two sampling sites during the sampling period (1.4 ± 1.4 m/s for BJ and 1.7 ± 1.1 m/s for BD, Fig. 3). Therefore, the spatial difference of $PM_{2.5}$ and the major components between the sampling sites of BJ and the other three could not be ascribed to the difference of the wind speeds. Because the information of PBL was not available in the region of Baoding, it is difficult to discuss the impact of PBL on the spatial difference of the pollutants. ~~were similar (Fig. 3) during the sampling period. However, there was obvious difference in the concentrations of OC, EC,~~ ~~NH_4^+, NO_3^-, SO_4^{2-}, Cl^- and K^+~~ ~~among the four sampling sites, ranked in order as BJ < WD < BD < DBT.~~ As listed in Table 2, the average concentration of the total species at DBT was about a factor of 2.7, 1.8 and 1.4 higher than those at BJ, WD and BD, respectively. The largest levels of the key species in $PM_{2.5}$ at DBT among the four sampling sites implied that the pollutants at the rural site were not through the air parcel transportation from its neighbor cities but mainly ascribed to the local emissions or formation. Vehicles and industries could be rationally excluded for explaining the largest levels of the key species in $PM_{2.5}$ at DBT, because these sources are very sparse in the rural area around DBT (See section 3.4). Compared with the cities, the distinct source for atmospheric pollutants at DBT in winter is the residential coal combustion which is prevailingly used for heating and cooking in rural areas of the Northern China. The emissions of various pollutants from residential coal combustion were very serious due to lack of any control measures, strong smoke could be seen in the chimney of the residential coal stoves. The emission factors of OC and EC from residential coal combustion were reported to be 0.47-7.82 g kg^{-1} coal and 0.028-2.75 g kg^{-1} coal, respectively (Chen et al., 2005; Zhang et al., 2008). The emission factors of various pollutants from a typical residential coal stove fueled with raw bituminous coal were also investigated in our group (Du et al., 2016; Liu et al., 2017) according to farmers' customary uses of coal stoves under the alternation cycles of flaming and smoldering. The emission factors of OC and EC under the entire combustion process could achieve to be 10.99 ± 0.95 g kg^{-1} coal and 0.84 ± 0.06 g kg^{-1} coal, respectively (Table 3). Considering the high density of farmers in the rural area, the largest levels of atmospheric OC and EC at DBT could be rationally ascribed to residential coal combustion. However, the proportion of the WSIs from residential coal combustion (Fig. 7a) were extremely low with respect to that of the atmosphere. Therefore, the largest levels of the key WSIs in $PM_{2.5}$ at DBT were suspected to the secondary formation via the heterogeneous or multiphase reactions which might be accelerated by the OC and EC particles (Han et al., 2013; Zhao et al., 2016) emitted from residential coal combustion.

Although the three sampling sites of DBT, WD and BD are closely adjacent, the lowest concentrations of the key species in $PM_{2.5}$ were observed at WD, which was probably ascribed to the replacement of coal with natural gas for the central heating in the county of WD (a main pipe of natural gas is just across the county), e.g., the average concentration of NO_2 was higher at WD than at BD, whereas the average concentration of SO_2 was on the contrary (Table 2). The city of BD and the county of WD are fully surrounded by high density of countryside, whereas the city of BJ is only neighbored with high density of countryside in the south-southeast-southwest directions, and thus the residential coal combustion was also suspected to be responsible for the remarkably higher concentrations of the key species in $PM_{2.5}$ at BD and WD than at BJ. To confirm the above assumptions, the chemical composition and source characteristics of the species in $PM_{2.5}$ were further analyzed in the following section.

3.3 Chemical composition of $PM_{2.5}$ at the four sampling sites

The average mass proportions of the species in $PM_{2.5}$ during the sampling period at the four sampling sites are illustrated in Fig. 7b. OC, EC, NH_4^+, NO_3^- and SO_4^{2-} were found to be the principal species, accounting for about 82 %-88 % of the total species in $PM_{2.5}$ at each sampling site, which were in line with previous studies (Zhao et al., 2013a; X. J. Zhao et al., 2013; Tian et al., 2014; Huang et al., 2014). As for the proportions of individual species, there were obvious differences between the sampling site of BJ and the sampling sites of BD, WD and DBT. The average mass proportions of OC and EC at BD, WD and DBT were very close, accounting for about 45.7 %-47.1 % and 9.0 %-10.4 % of the total species in $PM_{2.5}$, respectively, which were about 8 % for OC and 2 % for EC greater than those at BJ. In contrast to OC and EC, the average mass proportions of NO_3^- (10.1 %-10.8 %) and SO_4^{2-} (11.2 %-11.7 %) at BD, WD and DBT were about 5 % and 3 % less than those (15.1 % for NO_3^- and 14.0 % for SO_4^{2-}) at BJ, respectively. The obvious differences of the mass proportions of OC, EC, NO_3^- and SO_4^{2-} between the sampling site of BJ and the sampling sites of BD, WD and DBT indicated that the sources for the principal species at BJ were different from the other three sampling sites. The mass proportions of OC, EC, NO_3^- and SO_4^{2-} at BD and WD were very close to those at DBT, implying that residential coal combustion might also be the dominant source for the species in $PM_{2.5}$ at BD and WD. Residential sector (dominated by residential coal combustion) in the region of BTH during winter has been recognized as the dominant source for atmospheric OC and EC (Chen et al., 2017), which was estimated to contribute 85% and 65% of primary OC and EC emissions, respectively (J. Liu et al., 2016). Because the sampling sites of DBT, BD and WD are located in or fully surrounded by high density of countryside, the contribution of residential coal combustion to atmospheric OC and EC at DBT, BD and WD must evidently exceed the regional values estimated by J. Liu et al. (2016).

Although the mass proportions of NO_3^- and SO_4^{2-} were evidently lower at BD, WD and DBT than at BJ, the average mass concentrations of NO_3^- and SO_4^{2-} were on the contrary (Table 2). Atmospheric NO_3^- and SO_4^{2-} are mainly from secondary formation via heterogeneous, multiphase or gas-phase reactions which are depended on the concentrations of their precursors (NO_2 and SO_2) and OH radicals, the surface characteristics and areas of particles, and RH (Ravishankara, 1997; Wang et al., 2013; Quan et al., 2014; Nie et al., 2014; He et al., 2014; Yang et al., 2015; B. Zheng et al., 2015). The remarkably higher concentrations of NO_2, SO_2 and $PM_{2.5}$ at BD, WD and DBT (Liu et al., 2015) than at BJ (Table 2) favored secondary formation of NO_3^- and SO_4^{2-}, resulting in the relatively high concentrations of NO_3^- and SO_4^{2-}.

As shown in Fig. 8, the serious pollution episodes at BJ usually occurred during the periods with the air parcel from the southwest-south directions where farmers with high density reside, and thus residential coal combustion might also make evident contribution to atmospheric pollutants at BJ.

Because the species in $PM_{2.5}$ at BJ during the serious pollution episodes accounted for very large weight of their average concentrations, the proportions of the species in $PM_{2.5}$ were dominated by the serious pollution events. The highest NO_3^- and SO_4^{2-} proportions and the lowest OC and EC proportions at BJ among the four sampling sites might be partly ascribed to the conversions of NO_2 and SO_2 to NO_3^- and SO_4^{2-} during the air parcel transportation from the south-southwest directions. The contribution of the transportation to atmospheric OC and EC at BJ could be verified by the correlations between the OC/EC ratios and the $PM_{2.5}$ levels (Fig. 9). The OC/EC ratios (about 4.9 ± 0.7) at WD and DBT were almost independent of the $PM_{2.5}$ levels, whereas the OC/EC ratios at BJ and BD remarkably decreased with increasing the $PM_{2.5}$ levels and reached the almost same value (about 4.8 ± 0.5) as those at WD and DBT when the concentrations of $PM_{2.5}$ were above 150 μg m^{-3} (the serious pollution events). Because there were relatively sparse emissions from vehicles and industries at WD and DBT, the almost constant of OC/EC ratios under the different levels of $PM_{2.5}$ at WD and DBT further revealed that atmospheric OC and EC were dominated by the local residential coal combustion. The almost same OC/EC ratios at the four sampling sites with the concentrations of $PM_{2.5}$ greater than 150 μg m^{-3} indicated that the residential coal combustion also made dominant contribution to atmospheric OC and EC in the two cities during the severe pollution period. Our previous study (C. Liu et al., 2016) also found that the contribution from residential coal combustion to atmospheric VOCs increased from 23 % to 33 % with increasing pollution levels in Beijing.

It should be mentioned that the OC/EC ratios observed at DBT and WD were about a factor of 2.7 less than that (13.1) of the emission from the residential coal combustion, whereas at BJ and BD were too high to be explained by direct emissions from diesel (0.4-0.8) and gasoline (3.1) vehicles

(Shah et al., 2004; Geller et al., 2006). The OC emitted from the residential coal combustion might be easily degraded or volatilized in the atmosphere, resulting in the relatively low OC/EC ratios observed at DBT and WD. In China, aromatic compounds as typical pollutants from vehicle emissions are very reactive to make contribution to secondary organic aerosols (SOA) (Zhang et al., 2017), which was suspected to make evident contribution to the OC/EC ratios at BJ and BD when the atmospheric EC concentrations were relatively low. For example, the extremely high OC/EC ratios (> 6.0) at BJ and BD only occurred when the atmospheric EC concentrations were less than 3.2 μg m^{-3} at BJ and 5.4 μg m^{-3} at BD. Because the atmospheric EC concentrations at BJ and BD were about a factor of 4-6 greater during the serious pollution events than during the slight pollution events, the effect of SOA formation on the OC/EC ratios would become less during the serious pollution events if the SOA formation rate kept constant.

3.4 Correlations among the species in $PM_{2.5}$

The correlations among the WSIs, OC and EC in $PM_{2.5}$ at the four sampling sites are listed in Table 4. The number of the species involved in significant correlations evidently increased from the countryside to the cities and was 18, 28, 30 and 36 at DBT, WD, BD and BJ, respectively. The significant correlations among the species could be classified as three types: 1) associated with OC and EC; 2) associated with Ca^{2+} and Mg^{2+}; and 3) associated with K^+. Three types of significant correlations at DBT were independent of each other, whereas they were involved in interrelation more and more from WD to BJ. The independence for the three types of significant correlations at DBT further confirmed that residential coal combustion was preferentially dominant source for atmospheric OC and EC. The significant correlations among OC, EC, NO_3^-, NH_4^+ and Cl^- at DBT indicated that the OC and EC emitted from the residential coal combustion could quickly accelerate secondary formation of NO_3^-, NH_4^+ and Cl^- via heterogeneous or multiphase reactions of NO_x, NH_3 and HCl which have been verified to be emitted from the residential coal combustion (Wang et al., 2005; Shapiro et al., 2007; Bläsing and Müller, 2010; Meng et al., 2011; Zhang et al., 2013; Gao et al., 2015; Li et al., 2016a; Huang et al., 2016). The interrelation for the three types of significant correlations at WD, BD and BJ implied that complex sources including local emissions and regional transportation were dominant for atmospheric species in the cities. The species associated with Ca^{2+} and Mg^{2+} from construction and road dust (Liang et al., 2016) as well as the species associated with K^+ from biomass (municipal solid waste) burning (Gao et al., 2011; J. Li et al., 2014; Yao et al., 2016) in the cities would accumulate under stagnant air conditions at the earth surface, meanwhile the OC and EC concentrations could also increase due to the air parcel transportation with abundant OC and EC in the upper layer from the south-southwest directions (Fig. 8). It is interesting to note that the significant correlations among OC, EC, NO_3^-, NH_4^+ and Cl^- were found at the four sampling sites, whereas the significant correlation between OC (or EC) and SO_4^{2-} was only found at BJ. Because the sampling sites of DBT, WD and BD are close to the source of OC and EC from the residential coal combustion, the significant correlations among OC, EC, NO_3^-, NH_4^+ and Cl^- but the insignificant correlation between OC (or EC) and SO_4^{2-} implied that the formation rate of SO_4^{2-} via heterogeneous or multiphase reactions might be relatively slower than those of NO_3^-, NH_4^+ and Cl^-. The reactive uptake coefficients of SO_2 oxidation by O_3 were reported to be from 4.3×10^{-8} to 7×10^{-7} on different mineral aerosols and from 1×10^{-6} to 6×10^{-6} on soot particles (Wu et al., 2011; Song et al., 2012), which were at least one order of magnitude less than those of NO_2 (1.03×10^{-2}-3.43×10^{-3} on soot particles and 1.03×10^{-6}-1.2×10^{-5} on mineral aerosols) (Underwood et al., 2001; Esteve et al., 2004; Ma et al., 2011; Ma et al., 2017). The OC, EC and SO_2 emitted from the residential coal combustion experienced the relatively long period of excursion to be transported to Beijing, resulting in the significant correlation between OC (or EC) and SO_4^{2-} at BJ.

As listed in Table 5, the pronounced correlations for [As] vs. [Se] and [Cu] vs. [Zn] at the four sampling sites indicated that the two pairs of elements were from the common sources. Based on the remarkable elevations of As and Se near a coal-fired power plant with respect to the background site, Jayasekher (2009) pointed out that their significant correlation can be used as the tracer for coal combustion. Because Cu and Zn have been found to be mainly released from the additives of vehicle lubricating oils, brake and tire wear during transportation activities (Yu et al., 2013; Zhang et al., 2013; Tan et al., 2016), their significant correlation has been used as the tracer for vehicle emissions. Both coal combustion and vehicle emissions could make contribution to atmospheric Pb (Zhang et al., 2013; Gao et al., 2016), and thus the correlations for [Pb] vs. [Cu+Zn] and [Pb] vs. [As+Se] could reflect their local dominant sources. As shown in Fig. 10, the significant correlation between [Pb] and [Cu+Zn] but no correlation between [Pb] and [As+Se] were found at BJ, whereas the correlations at the rural site of DBT were on the contrary, indicating that atmospheric Pb, Cu and Zn at BJ were mainly related to the vehicle emissions and atmospheric Pb, As and Se at DBT were dominated by residential coal combustion. Because the sampling sites of BD and WD were affected by both vehicle emissions and residential coal combustion, the significant correlations between [Pb] and [Cu+Zn] as well as [Pb] and [As+Se] were found at the two sampling sites. Although there was no correlation between [Pb] and [As+Se] at BJ, the contribution of residential coal combustion to atmospheric $PM_{2.5}$ in the city of BJ could not be excluded because the trace elements from coal combustion are mainly present in relatively large particles (0.8-2.5 μm) which might quickly deposit near their sources (Wang et al., 2008).

3.5 Source apportionment of $PM_{2.5}$ at the four sampling sites

The source characteristics of $PM_{2.5}$ at the four sampling sites were analyzed by the CMC method which has been described in detail in section 2.3. The average proportions of the species from different sources in $PM_{2.5}$ during the sampling period at the four sampling sites are comparatively shown in Fig. 11. It is evident that secondary aerosols (SIA + SOC) accounted for the largest proportion (about 32-41 %) in $PM_{2.5}$, followed by POC (about 24-28 %), EC (about 6-8 %), mineral dust (about 2-8 %) and Cl^{-}_{cc} (about 2-5 %) at the four sampling sites. The proportion of mineral dust was the highest at BJ and the lowest at DBT among the four sampling sites, whereas the proportion of Cl^{-}_{cc} was on the contrary. Because the concentrations of the mineral dust compounds were much higher under stagnant weather condition than under clean days at BJ, the remarkably high proportion of mineral dust at BJ was mainly ascribed to the emissions from road dust and construction (Liang et al., 2016) during the sampling period. The obviously high proportion of Cl^{-}_{cc} at DBT was ascribed to the emission from residential coal combustion (Shen et al., 2016). In addition, the proportions of TEO, K^{+}_{bb} and Cl^{-}_{ss} were less than about 2 %, which were insignificant to the sources of $PM_{2.5}$ at the four sampling sites during the sampling period.

Atmospheric Primary Organic Matters (POM) and Cl^{-}_{cc} at the four sampling sites could be estimated based on POM≈POC × 1.6 (Cheung et al., 2005; Hsu et al., 2010b; Han et al., 2015) and the formulas (1)-(4), respectively. The sum of POM, EC and Cl^{-}_{cc} at DBT was assumed to be solely from residential coal combustion, accounting for about 58% in $PM_{2.5}$ (Fig. 12). Assuming that the ratio of Cl^{-}_{cc} to the sum of POM, EC and Cl^{-}_{cc} was constant for coal combustion at the four sampling sites, the primary contribution of coal combustion to atmospheric $PM_{2.5}$ at BJ, BD and WD could be estimated to be 32 %, 49 % and 43 % (Fig. 12), respectively. The annual residential coal consumption mainly focused on the four months in winter, accounting for about 11 % of the total coal consumption in the region of BTH. Because the emission factor of $PM_{2.5}$ from residential coal combustion (about 1054-12910 mg kg^{-1}) was about 1-3 orders of magnitude greater than those from industry boilers or coal power plants (about 16-100 mg kg^{-1}) (Chen et al., 2005; Zhang et al., 2008), the estimated proportions of the contribution of coal combustion to atmospheric $PM_{2.5}$ at the four sampling sites during the winter were mainly ascribed to residential coal combustion. If only the primary $PM_{2.5}$ was considered, the contribution of residential coal combustion to the primary $PM_{2.5}$ at BJ would achieve to be about 59 % which was in line with the value of 57 % estimated by J. Liu et al. (2016) for the winter of 2010 in Beijing.

4 Conclusions

Based on the comprehensive analysis of the levels, composition characteristics, the correlations of the key species in $PM_{2.5}$ and the back trajectories, residential coal combustion in the North China during winter was found not only to be the dominant source for atmospheric OC, EC, Cl^-, NO_3^-, SO_4^{2-} and NH_4^+ in rural areas but also to make evident contribution to the species in cities. According to the CMC method, the contributions of the primary particle emission from residential coal combustion to atmospheric $PM_{2.5}$ at BJ, BD, WD and DBT during winter were estimated to be 32 %, 49 %, 43 % and 58 %, respectively. Therefore, strict control measures should be implemented for the emissions from residential coal combustion to mitigate the currently serious $PM_{2.5}$ pollution during the winter in the North China.

Author contribution

Y. J. Mu designed the experiments and prepared the manuscript. **P. F. Liu** and **C. L. Zhang** carried out the experiments and prepared the manuscript, and contributed equally to this work. **C. Y. Xue**

~~and C. L. Zhang~~ carried out the experiments. **J. F. Liu**, **Y. Y. Zhang**, **D. Tian** and **C. Ye** were involved in part of the work. **H. X. Zhang** provided the meteorological data and trace gases in Beijing. **J. Guan** provided the meteorological data and trace gases in Baoding and Wangdu.

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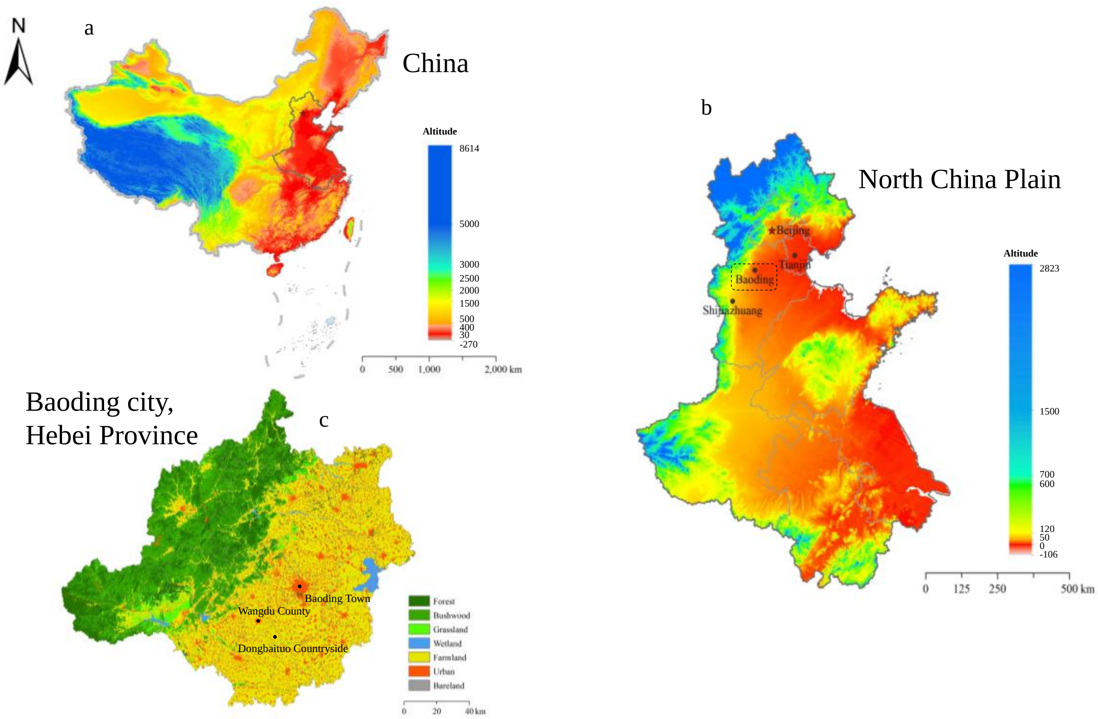


Figure 1. China (a), the North China Plain (b) and Baoding city in Hebei Province (c). The locations of sampling sites (BJ, BD, WD and DBT) as well as Tianjin municipality and Shijiazhuang as provincial capital of Hebei are marked.

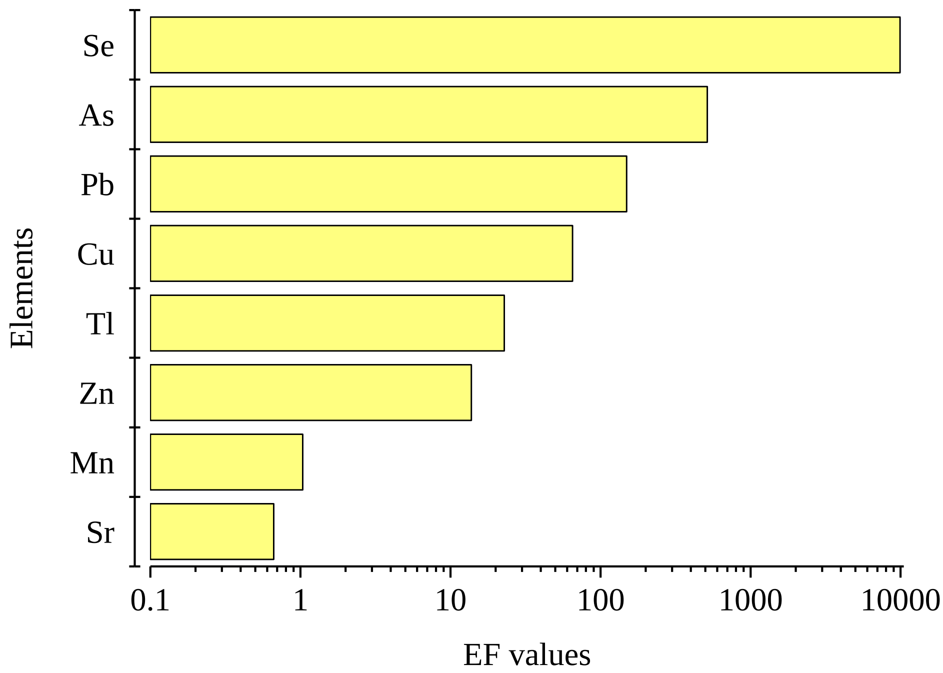


Figure 2. Enrichment factor values for trace elements in $PM_{2.5}$.

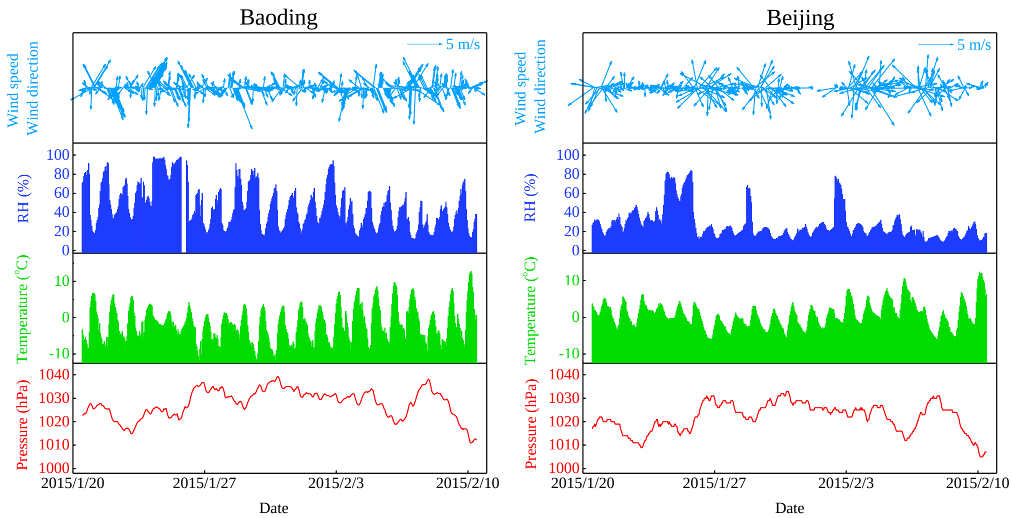


Figure 3. The wind speed, wind direction, RH, temperature and barometric pressure at BD and BJ during the sampling period in the winter of 2015.

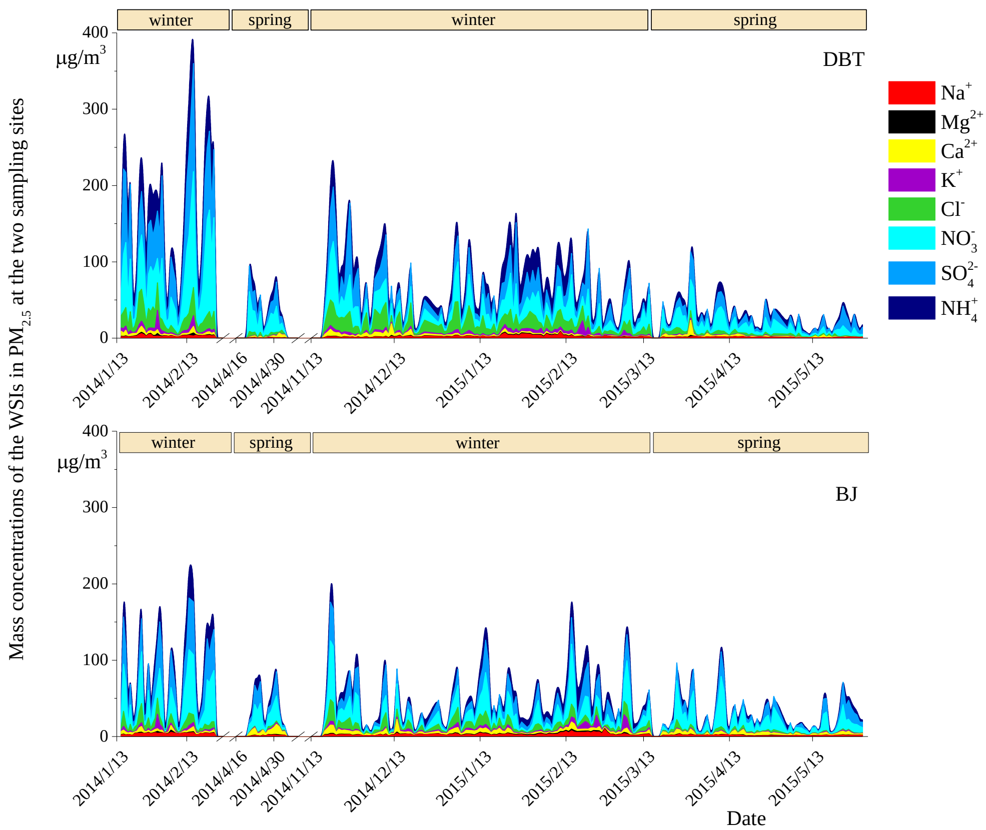
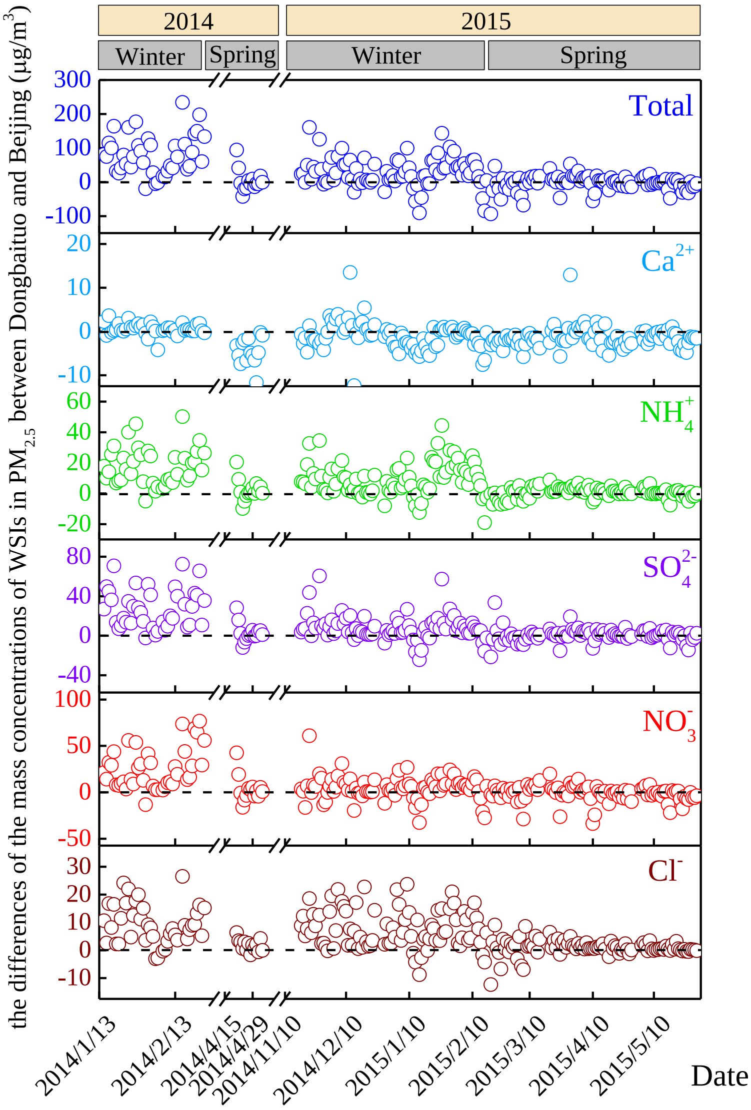


Figure 4. The mass concentrations of the WSIs in $PM_{2.5}$ at DBT and BJ during the sampling period in the winters and springs of 2014-2015.



1055

1056 **Figure 5.** The D-values of the mass concentrations of WSIs in $PM_{2.5}$ between DBT and BJ during

1057 the sampling period in the winters and springs of 2014-2015.

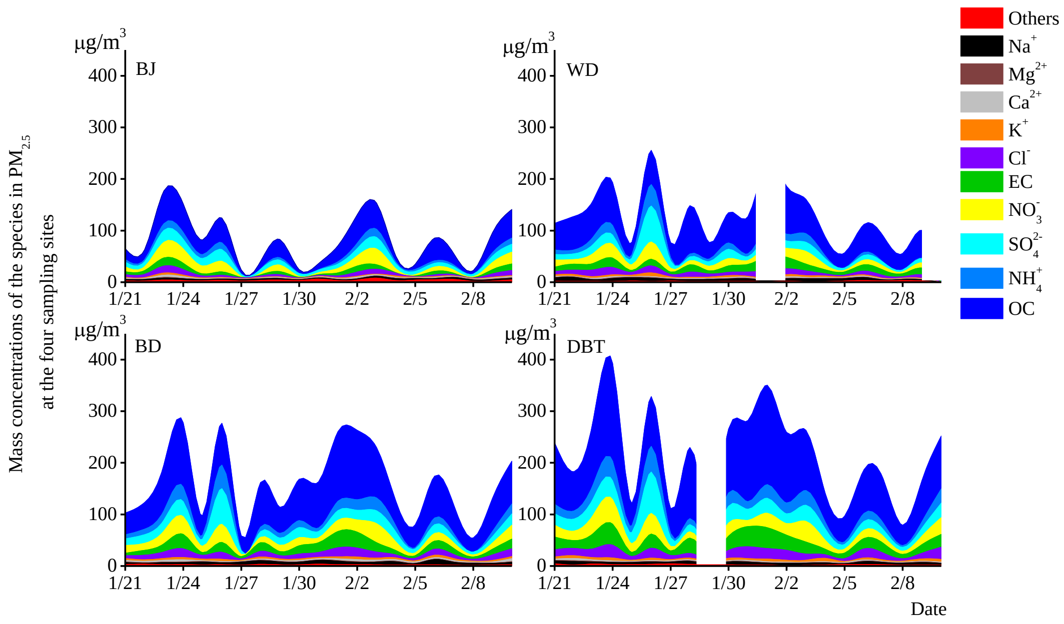


Figure 6. Daily variation of the species in $PM_{2.5}$ at the four sampling sites during the sampling period in the winter of 2015.

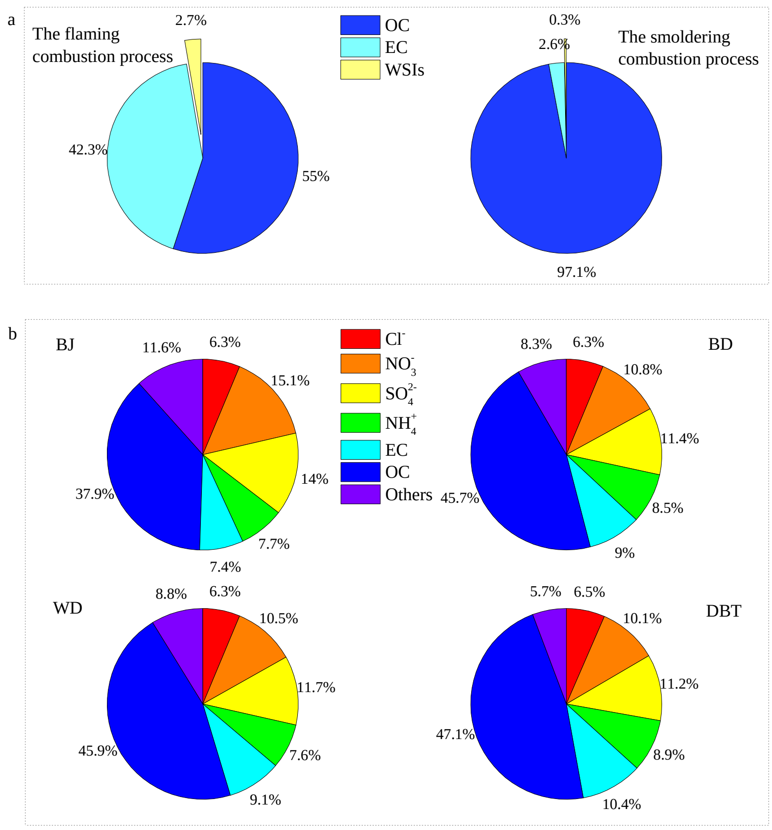


Figure 7. The mass proportions of OC, EC and WSIs from residential coal combustion under the flaming and smoldering combustion processes (a), and the average mass proportions of the typical

species in $PM_{2.5}$ at the four sampling sites during the sampling period in the winter of 2015 (b).

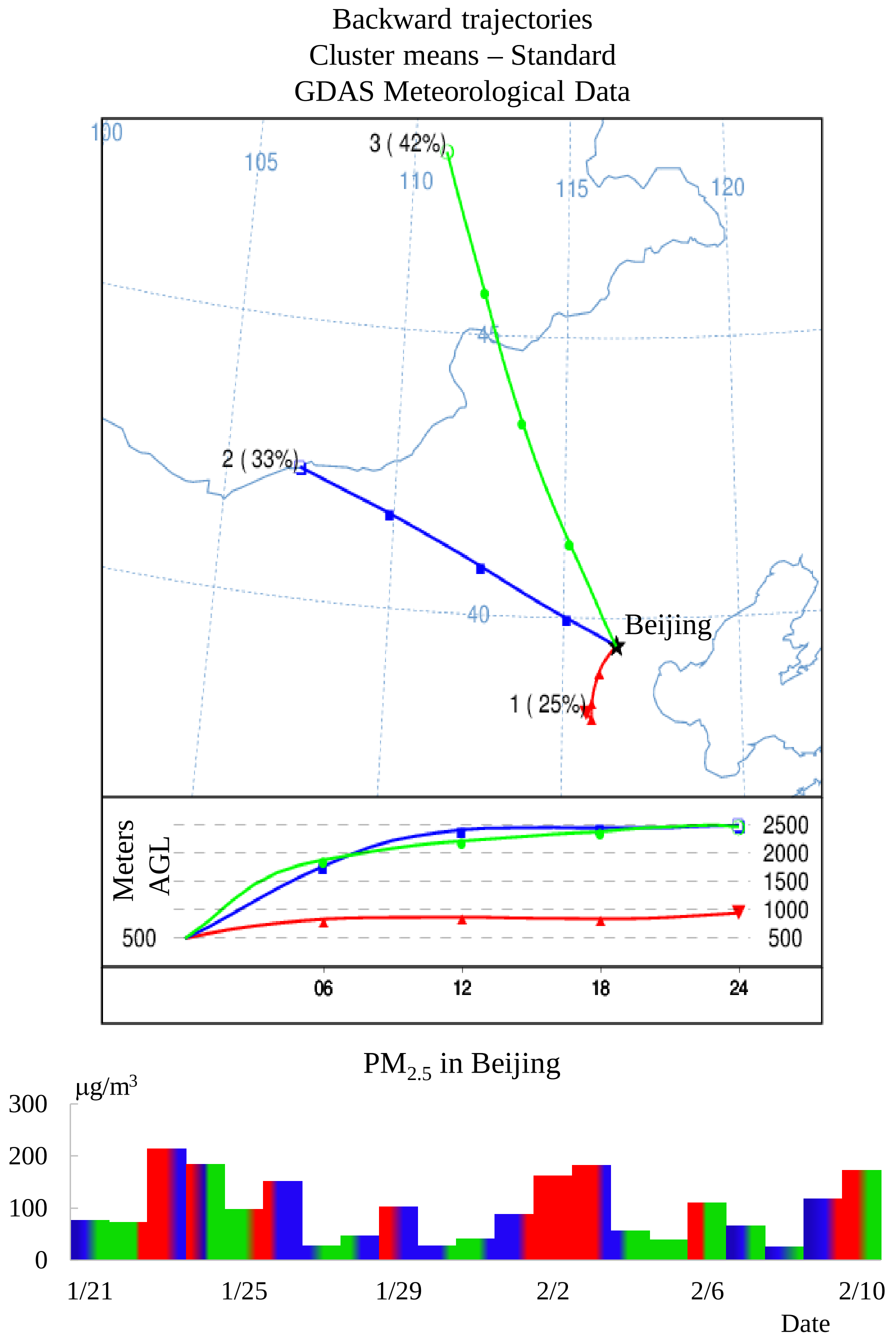


Figure 8. The back trajectory cluster analysis and the corresponding $PM_{2.5}$ concentrations in Beijing during the sampling period in the winter of 2015.

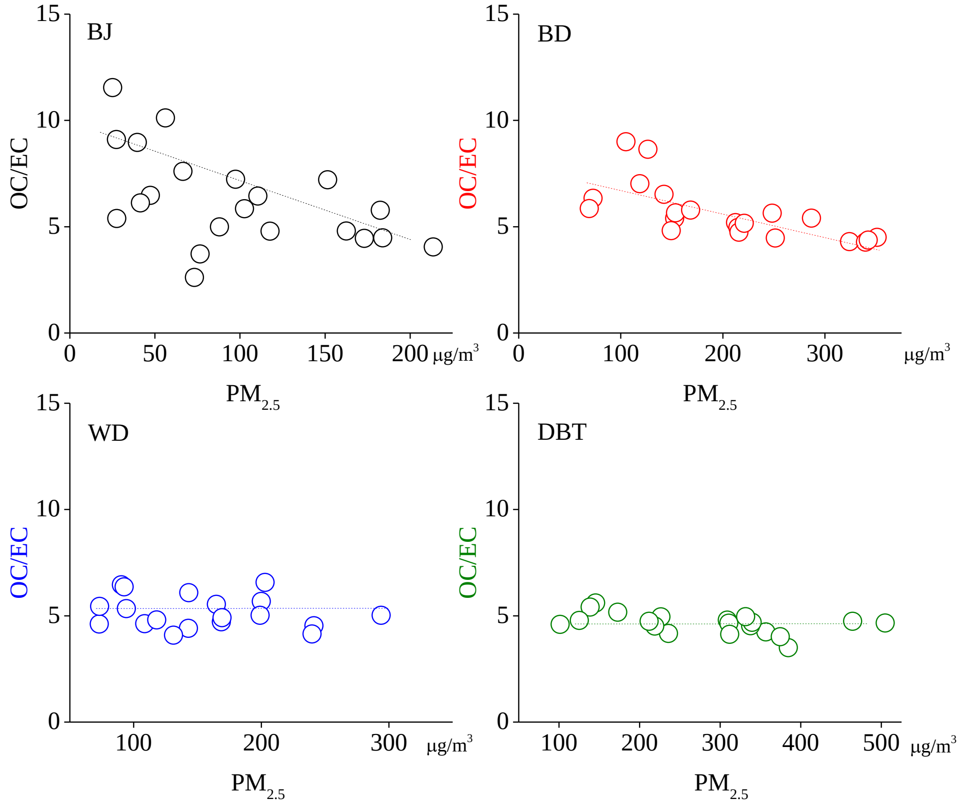


Figure 9. The correlations between the OC/EC ratios and the PM$_{2.5}$ concentrations at the four sampling sites during the sampling period in the winter of 2015.

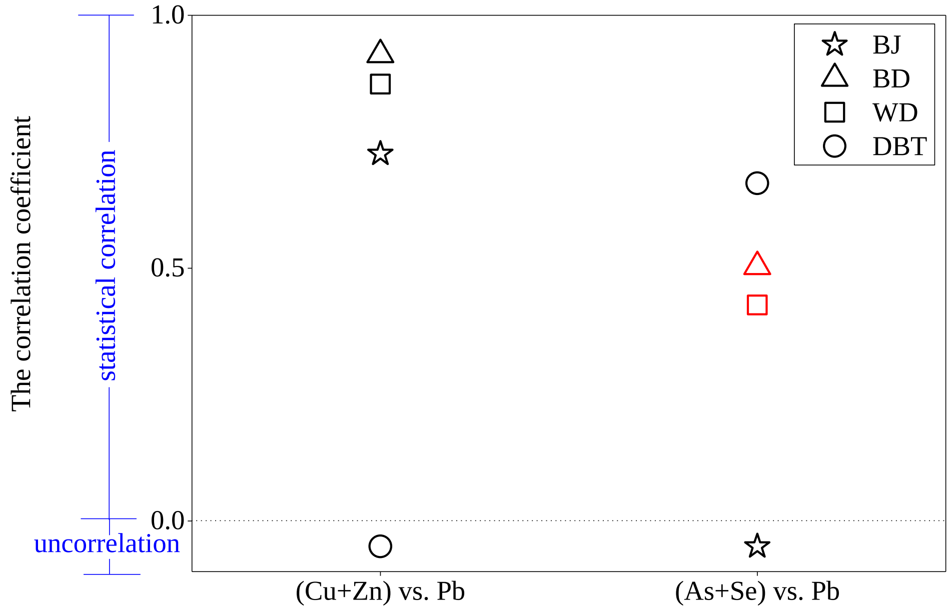


Figure 10. The statistical correlations for [Cu+Zn] vs. [Pb] and [As+Se] vs. [Pb] in PM$_{2.5}$ at the four sampling sites during the sampling period in the winter of 2015. The uncorrelated results are

also marked below zero of Y axis. The red and black symbols represent for $p < 0.05$ and $p < 0.01$, respectively.

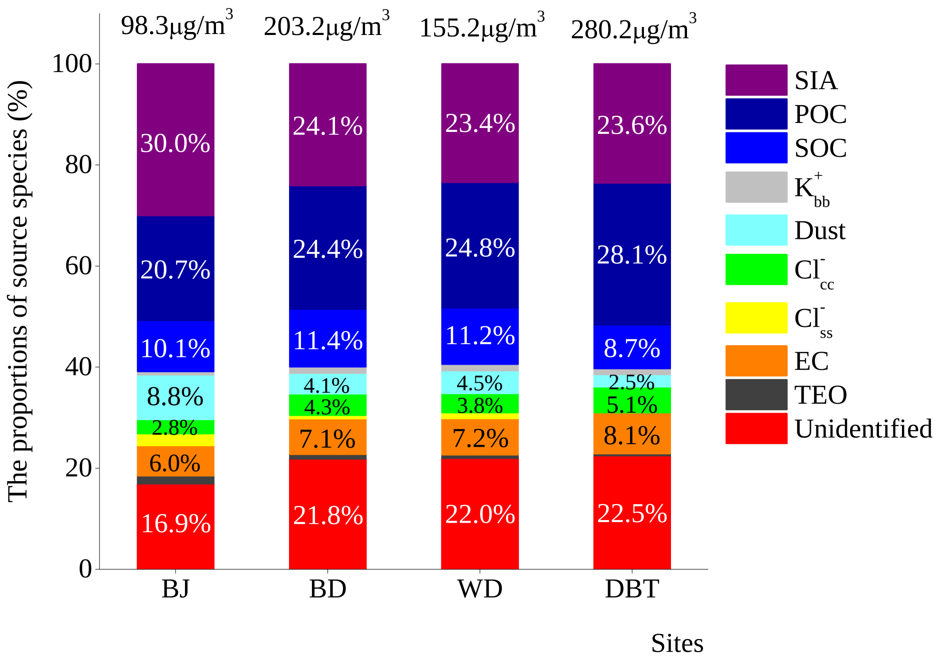


Figure 11. The proportions of source species under the constructed chemical mass closures for $PM_{2.5}$ at the four sampling sites during the sampling period in the winter of 2015. Average mass concentrations of $PM_{2.5}$ at each sampling site, including all of source species and unidentified fractions, are also marked at the top of bar charts.

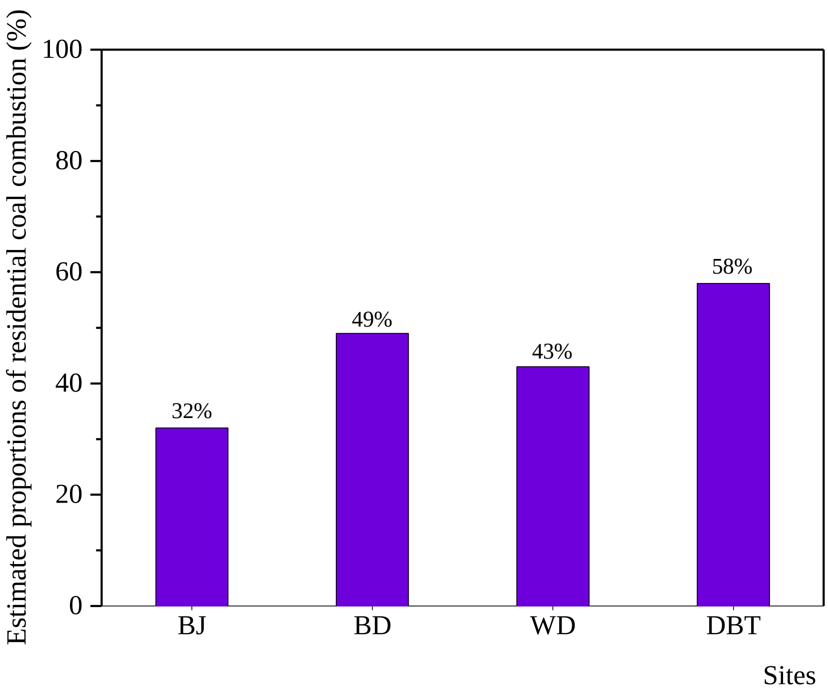


Figure 12. The estimated contributions of coal combustion to the $PM_{2.5}$ at the four sampling sites during the sampling period in the winter of 2015.

Table 1. The average mass concentrations of WSIs in $PM_{2.5}$ at DBT and BJ during the sampling period in the winters and springs of 2014-2015 ($\mu g\ m^{-3}$).

WSIs	spring		winter	
	DBT	BJ	DBT	BJ
Na^+	1.0 ± 0.5	1.4 ± 0.5	2.4 ± 1.3	3.1 ± 1.4
Mg^{2+}	0.2 ± 0.2	0.3 ± 0.2	0.7 ± 0.5	0.8 ± 0.7
Ca^{2+}	1.7 ± 2.4	3.4 ± 2.5	2.6 ± 2.1	3.4 ± 2.3
K^+	0.5 ± 0.5	0.7 ± 0.4	3.2 ± 3.0	3.0 ± 6.0
NH_4^+	6.1 ± 5.1	4.8 ± 4.7	23.1 ± 17.9	13.2 ± 11.6
NO_3^-	12.5 ± 11.2	13.6 ± 13.2	28.4 ± 28.0	19.0 ± 20.0
SO_4^{2-}	10.5 ± 8.2	9.2 ± 8.6	29.0 ± 28.1	17.4 ± 16.5
Cl^-	2.9 ± 2.2	1.8 ± 1.6	14.1 ± 9.4	7.2 ± 6.0
Total	35.3 ± 26.7	35.1 ± 28.7	103.3 ± 81.3	67.0 ± 55.2

Table 2. The average mass concentrations (Mean ± SD) of $PM_{2.5}$ species, NO_2 and SO_2 at the four sampling sites during the sampling period in the winter of 2015 ($\mu g\ m^{-3}$).

Species	BJ	BD	WD	DBT
Na^+	2.5 ± 0.7	4.8 ± 2.0	4.5 ± 1.7	4.3 ± 1.2
Mg^{2+}	0.3 ± 0.1	0.4 ± 0.1	0.3 ± 0.1	0.4 ± 0.2
Ca^{2+}	1.8 ± 0.9	2.6 ± 0.8	1.7 ± 0.6	2.0 ± 0.8
K^+	0.7 ± 0.8	2.5 ± 1.0	2.0 ± 1.4	3.1 ± 1.3
NH_4^+	6.0 ± 5.0	13.3 ± 11.0	9.3 ± 9.5	18.7 ± 11.7
NO_3^-	11.7 ± 10.1	16.6 ± 10.3	13.0 ± 8.2	21.0 ± 12.2
SO_4^{2-}	11.2 ± 6.5	18.1 ± 14.1	14.5 ± 14.5	24.1 ± 16.1
Cl^-	5.0 ± 3.6	9.5 ± 4.2	7.8 ± 3.5	13.4 ± 6.0
OC	28.6 ± 19.6	70.2 ± 31.2	57.2 ± 21.3	100.0 ± 42.9
EC	5.5 ± 4.5	13.5 ± 7.8	11.4 ± 4.7	21.6 ± 10.2
Al	0.6 ± 0.8	0.6 ± 0.1	0.5 ± 0.2	0.5 ± 0.1
Mn	0.1 ± 0.1	0.1 ± 0.1	0.1 ± 0.1	0.2 ± 0.3
Fe	2.1 ± 0.8	0.6 ± 0.2	0.8 ± 0.6	1.3 ± 0.6
Cu	0.6 ± 0.3	0.3 ± 0.1	0.2 ± 0.1	0.1 ± 0.1
Zn	0.1 ± 0.1	0.2 ± 0.1	0.1 ± 0.1	0.1 ± 0.1
As	0.1 ± 0.1	0.3 ± 0.1	0.2 ± 0.1	0.1 ± 0.1
Se	0.1 ± 0.0	0.1 ± 0.1	0.1 ± 0.0	0.1 ± 0.0
Sr	0.0 ± 0.0	0.1 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
Tl	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
Pb	0.2 ± 0.2	0.4 ± 0.3	0.2 ± 0.1	0.3 ± 0.1
The total	80.1 ± 47.7	159.5 ± 70.3	121.7 ± 51.8	218.4 ± 87.1
NO_2	36.5 ± 17.4	60.4 ± 23.4	76.1 ± 19.2	-
SO_2	63.9 ± 31.7	181.7 ± 62.4	101.3 ± 39.4	-

Table 3. The emission factors (Mean ± SD) (g kg^{-1} coal) of OC and EC from residential coal combustion during the flaming combustion process, the smoldering combustion process and the entire combustion process.

Emission factors	the flaming combustion process	the smoldering combustion process	the entire combustion process
OC	1.83 ± 1.19	17.11 ± 0.79	10.99 ± 0.95
EC	1.40 ± 0.11	0.46 ± 0.03	0.84 ± 0.06

Table 4. The correlations of several typical species in $PM_{2.5}$ at the four sampling sites during the sampling period in the winter of 2015.

n=21	BJ								
	Mg^{2+}	Ca^{2+}	K^+	Cl^-	NO_3^-	SO_4^{2-}	NH_4^+	OC	EC
Mg^{2+}	1								
Ca^{2+}	0.895**	1							
K^+	0.634**	0.862**	1						
Cl^-	0.856**	0.899**	0.791**	1					
NO_3^-	0.803**	0.768**	0.637**	0.905**	1				
SO_4^{2-}	0.679**	0.660**	0.590**	0.804**	0.950**	1			
NH_4^+	0.718**	0.667**	0.543*	0.834**	0.971**	0.959**	1		
OC	0.845**	0.751**	0.560**	0.848**	0.919**	0.838**	0.895**	1	
EC	0.849**	0.851**	0.679**	0.932**	0.877**	0.769**	0.823**	0.936**	1
n=21	BD								
	Mg^{2+}	Ca^{2+}	K^+	Cl^-	NO_3^-	SO_4^{2-}	NH_4^+	OC	EC
Mg^{2+}	1								
Ca^{2+}	0.805**	1							
K^+	0.697**	0.556**	1						
Cl^-	0.714**	0.659**	0.789**	1					
NO_3^-	0.554**	0.560**	0.675**	0.757**	1				
SO_4^{2-}	0.022	0.107	0.491*	0.499*	0.764**	1			
NH_4^+	0.315	0.331	0.659**	0.721**	0.920**	0.941**	1		
OC	0.743**	0.576**	0.705**	0.936**	0.674**	0.369	0.614**	1	
EC	0.698**	0.560**	0.702**	0.939**	0.660**	0.410	0.633**	0.984**	1
n=19	WD								
	Mg^{2+}	Ca^{2+}	K^+	Cl^-	NO_3^-	SO_4^{2-}	NH_4^+	OC	EC
Mg^{2+}	1								
Ca^{2+}	0.897**	1							
K^+	0.226	0.457*	1						
Cl^-	0.532*	0.663**	0.598**	1					
NO_3^-	0.468*	0.677**	0.712**	0.796**	1				
SO_4^{2-}	0.097	0.358	0.874**	0.552*	0.770**	1			
NH_4^+	0.306	0.563**	0.906**	0.735**	0.901**	0.945**	1		
OC	0.463*	0.543*	0.372	0.816**	0.471*	0.222	0.581*	1	
EC	0.553*	0.638**	0.339	0.763**	0.510*	0.214	0.565*	0.925**	1

n=20	DBT								
	Mg^{2+}	Ca^{2+}	K^+	Cl^-	NO_3^-	SO_4^{2-}	NH_4^+	OC	EC
Mg^{2+}	1								
Ca^{2+}	0.721**	1							
K^+	0.191	0.407	1						
Cl^-	-0.061	0.316	0.519*	1					
NO_3^-	-0.241	0.161	0.579**	0.642**	1				
SO_4^{2-}	-0.133	0.109	0.458*	0.482*	0.744**	1			
NH_4^+	-0.223	0.125	0.558*	0.697**	0.928**	0.914**	1		
OC	0.067	0.159	0.419	0.772**	0.570**	0.293	0.557*	1	
EC	0.051	0.169	0.419	0.838**	0.585**	0.400	0.624**	0.977**	1

*, ** represent for $p < 0.05$ and $p < 0.01$, respectively.

Table 5. The correlations between [Zn] vs. [Cu] and [As] vs. [Se] in $PM_{2.5}$ at the four sampling sites during the sampling period in the winter of 2015.

Elements	BJ (n=21)	BD (n=21)	WD (n=19)	DBT (n=20)
[Zn] vs. [Cu]	0.607**	0.479*	0.620*	0.659**
[As] vs. [Se]	0.662**	0.664**	0.959**	0.871**

*, ** represent for $p < 0.05$ and $p < 0.01$, respectively.