



1 The contribution of residential coal combustion to atmospheric PM<sub>2.5</sub>  
2 in the North China during winter

3 Pengfei Liu<sup>1, 3</sup>, Chenglong Zhang<sup>1, 3</sup>, Chaoyang Xue<sup>1, 3</sup>, Yujing Mu<sup>1, 2, 3</sup>, Junfeng Liu<sup>1, 3</sup>,  
4 Yuanyuan Zhang<sup>1, 3</sup>, Di Tian<sup>1, 3</sup>, Can Ye<sup>1, 3</sup>, Hongxing Zhang<sup>1, 4</sup>, Jian Guan<sup>5</sup>

5 <sup>1</sup> Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, 100085, China

6 <sup>2</sup> Center for Excellence in Urban Atmospheric Environment, Institute of Urban Environment, Chinese Academy of  
7 Sciences, Xiamen, 361021, China

8 <sup>3</sup> University of Chinese Academy of Sciences, Beijing, 100049, China

9 <sup>4</sup> Beijing Urban Ecosystem Research Station, Beijing, 100085, China

10 <sup>5</sup> Environment Monitoring Station of Baoding City, Hebei, 071000, China

11 Correspondence to: **Y. J. Mu** ([yjmu@rcees.ac.cn](mailto:yjmu@rcees.ac.cn))

12 Abstract: The vast area in the North China, especially during wintertime, is currently suffering  
13 from severe haze events due to the high levels of atmospheric PM<sub>2.5</sub>. To recognize the reasons for  
14 the high levels of PM<sub>2.5</sub>, daily samples of PM<sub>2.5</sub> were simultaneously collected at the four  
15 sampling sites of Beijing City (BJ), Baoding City (BD), Wangdu County (WD) and Dongbaituo  
16 Countryside (DBT) during the winters and springs of 2014-2015. The concentrations of the typical  
17 water-soluble ions (WSIs, such as Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and NH<sub>4</sub><sup>+</sup>) at DBT were found to be  
18 remarkably higher than those at BJ in the two winters but almost the same as those at BJ in the  
19 two springs. The evidently greater concentrations of OC, EC and secondary inorganic ions (NO<sub>3</sub><sup>-</sup>,  
20 SO<sub>4</sub><sup>2-</sup>, NH<sub>4</sub><sup>+</sup> and Cl<sup>-</sup>) at DBT than at WD, BD and BJ during the winter of 2015 indicated that the  
21 pollutants in the rural area were not due to transportation from its neighbor cities but dominated by  
22 local emissions. As the distinct source for atmospheric OC and EC in the rural area, the residential  
23 coal combustion also made contribution to secondary inorganic ions through the emissions of their  
24 precursors (NO<sub>x</sub>, SO<sub>2</sub>, NH<sub>3</sub> and HCl) as well as heterogeneous or multiphase reactions on the  
25 surface of OC and EC. The average mass proportions of OC, EC, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> at BD and WD  
26 were found to be very close to those at DBT, but evidently different from those at BJ, implying  
27 that the pollutants in the cities of WD and BD which are fully surrounded by the countryside were  
28 strongly affected by the residential coal combustion. The OC/EC ratios at the four sampling sites  
29 became the almost same value of 4.8 when the concentrations of PM<sub>2.5</sub> were greater than 150 μg  
30 m<sup>-3</sup>, suggesting that the residential coal combustion could also make dominant contribution to  
31 atmospheric PM<sub>2.5</sub> at BJ during the severe pollution period when the air parcels were usually from  
32 southwest–south regions where high density of farmers reside. The evident increase of the number  
33 of the species involved in significant correlations from the countryside to the cities further  
34 confirmed that residential coal combustion was preferentially dominant source for the key species  
35 in the rural area whereas the complex sources including local emissions and regional  
36 transportation were dominant for atmospheric species in the cities. The significant correlations  
37 among OC, EC, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, and NH<sub>4</sub><sup>+</sup> were found at the four sampling sites but only significant  
38 correlation between OC (or EC) and SO<sub>4</sub><sup>2-</sup> was found at BJ, implying that the formation rate of  
39 SO<sub>4</sub><sup>2-</sup> via heterogeneous or multiphase reactions might be relatively slower than those of NO<sub>3</sub><sup>-</sup>,  
40 NH<sub>4</sub><sup>+</sup> and Cl<sup>-</sup>. Based on the chemical mass closure (CMC) method, the contributions of the



41 primary particle emission from residential coal combustion to atmospheric PM<sub>2.5</sub> at BJ, BD, WD  
42 and DBT were estimated to be 32 %, 49 %, 43 % and 58 %, respectively.

### 43 **1 Introduction**

44 In recent years, the vast area in the North China is frequently suffering from severe haze pollution  
45 (Chan and Yao, 2008; Zhang et al., 2012; Zhang et al., 2015), which has aroused great attention to  
46 the public (Guo et al., 2014; Huang et al., 2014; Cheng et al., 2016; Wang et al., 2016; J. Liu et al.,  
47 2016). The severe haze pollution is mainly due to the high level of fine particulate matters with  
48 dynamic diameter less than 2.5µm (PM<sub>2.5</sub>) (Huang et al., 2014; P. Liu et al., 2016). PM<sub>2.5</sub> can  
49 reduce atmospheric visibility by absorbing or scattering the incident light (Buseck and Posfai,  
50 1999; Cheng et al., 2006) and increase morbidity and mortality by penetrating the human bronchi  
51 and lungs (Nel, 2005; Poschl, 2005; Peplow, 2014).

52 To alleviate the serious haze pollution problems, the Chinese government has performed a series  
53 of control measures for major pollution sources (Zhang et al., 2012; J. Liu et al., 2016; Li et al.,  
54 2016b; Wen et al., 2016). For example, coal-fired power plants have been forced to install flue gas  
55 desulfurization and denitration (Zhang et al., 2012; Chen et al., 2014), coal has been replaced with  
56 natural gas and electricity in megacities (Wang et al., 2009; Duan et al., 2012; Zhao et al., 2013a;  
57 Tan et al., 2016), stricter emission standards have been implemented for vehicles and industrial  
58 boilers (Zhang et al., 2012; Tang et al., 2016) and so on, resulting in the decrease trend of primary  
59 pollutants including PM<sub>2.5</sub> in recent years (Ma et al., 2016; Wen et al., 2016; Zhang et al., 2016).  
60 However, the PM<sub>2.5</sub> levels still achieved to be above 1000 µg m<sup>-3</sup> in some areas of  
61 Beijing-Tianjin-Hebei (BTH) region during the period of the red alert for haze in December 2016  
62 ([http://english.mep.gov.cn/News\\_service/media\\_news/201612/t20161220\\_369317.shtml](http://english.mep.gov.cn/News_service/media_news/201612/t20161220_369317.shtml)) when  
63 the stricter control measures (e.g. stop production for industries and construction, and the odd and



64 even number rule) had been performed (Y. Li et al., 2016), implying that sources other than  
65 industries, construction and vehicles might make dominant contribution to atmospheric PM<sub>2.5</sub> in  
66 the region. Residential coal combustion which is prevailing for heating during winter in the region  
67 was suspected to be a dominant source for atmospheric PM<sub>2.5</sub>. Although annual residential coal  
68 consumption (about 4,200,000 kg) in BTH region only accounts for small fraction (about 11 %) of  
69 the total coal consumption ([http://www.qstheory.cn/st/dfst/201306/t20130607\\_238302.htm](http://www.qstheory.cn/st/dfst/201306/t20130607_238302.htm)), the  
70 emission factors of primary pollutants including PM<sub>2.5</sub> from the residential coal combustion have  
71 been found to be about 1-3 orders of magnitude greater than those from coal combustion of  
72 industries and power plants (Revuelta et al., 1999; Chen et al., 2005; Xu et al., 2006; Zhang et al.,  
73 2008; Geng et al., 2014; Yang et al., 2016). In addition, annual residential coal consumption  
74 mainly focuses on the four months in winter. Although the Chinese government has implemented  
75 control measures for residential coal combustion (e.g. replacement of traditional coal stoves by  
76 new stoves, bituminous coal by anthracite, and coal by electricity and natural gas), the promotion  
77 strength of the control measures was still very limited. Additionally, the promotion new stoves are  
78 still with strong smoke emission due to lack of clean combustion technique, and the anthracite is  
79 not welcomed by farmers because of its extremely slow combustion rate in comparison with  
80 bituminous coal.

81 There were few studies focusing on the influence of residential coal combustion on atmospheric  
82 particles in the North China. W. Li et al. (2014) concluded that strong sources for PM<sub>10</sub> in rural  
83 residential areas were from household solid fuel combustion, based on annual mean PM<sub>10</sub>  
84 concentrations observed in urban regions ( $180 \pm 171 \mu\text{g m}^{-3}$ ) and rural villages ( $182 \pm 154 \mu\text{g m}^{-3}$ )  
85 in the northern China. Duan et al. (2012) inferred that the lower OC/EC ratios at the rural site than



86 at the urban site was ascribed to coal combustion prevailed in the rural area. Our previous study  
87 revealed that residential coal combustion made evident contribution to atmospheric water-soluble  
88 ions (WSIs) in Beijing (P. Liu et al., 2016). Based on Weather Research and Forecasting model  
89 coupled with Chemistry, J. Liu et al. (2016) recently estimated that the residential sources (solid  
90 fuel) contributed 32 % and 53 % of the primary  $PM_{2.5}$  emissions in the BTH region during the  
91 whole year and during the winter of 2010, respectively.

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

## 98 **2 Materials and methods**

### 99 **2.1 Sampling sites**

100 The two sampling sites in Beijing City and Dongbaituo Countryside, which have been described  
101 in detail by our previous study (P. Liu et al., 2016), were selected on a rooftop (approximately 25  
102 m and 5 m above ground, respectively) of the Research Center for Eco-Environment Sciences,  
103 Chinese Academy of Sciences (RCEES, CAS) and a field station in the agricultural field of  
104 Dongbaituo village, Baoding, Hebei Province, respectively. Another two sampling sites in  
105 Baoding City and Wangdu County were both chosen on the rooftop of local environmental  
106 monitor station (about 30 m and 20 m above ground, respectively), which are both located in the  
107 center of the cities and surrounded by some commercial and residential areas. The detailed



108 location of the four sampling sites is presented in Fig. 1 and the distances between Beijing and  
109 Baoding, Baoding and Wangdu, Wangdu and Dongbaituo are about 156 km, 36 km and 12 km,  
110 respectively. Thereafter, the sampling sites of Beijing, Baoding, Wangdu and Dongbaituo are  
111 abbreviated as BJ, BD, WD and DBT, respectively.

## 112 2.2 Sample collection and analysis

113 PM<sub>2.5</sub> samples at BJ and DBT were collected simultaneously on PTFE filters (90 mm, Millipore)  
114 by medium-volume PM<sub>2.5</sub> samplers (LaoYing-2034) at a flow rate of 100 L min<sup>-1</sup> from January 15,  
115 2014 to May 31, 2015, in winter (January 15, 2014-February 25, 2014, November 18, 2014-January  
116 20, 2015 and February 11, 2015-March 15, 2015) and spring (April 21, 2014-May 4, 2014 and  
117 March 20, 2015-May 31, 2015). An enhanced observation which added the other two sampling  
118 sites of BD and WD was carried and PM<sub>2.5</sub> samples at the four sampling sites were collected in the  
119 same way on the quartz fiber filters (90 mm, Munktell) from January 21 to February 10, 2015. The  
120 sampling duration was 24 h (from 15:00 p.m. to 15:00 p.m. of the following day in local time  
121 (UTC + 8)). All the samples were put in appropriate dishes (90 mm, Millipore) after sampling  
122 and preserved in a refrigerator immediately until analysis.

123 As for the quartz fiber filters, half of each filter was extracted ultrasonically with 10 mL ultrapure  
124 water for half an hour. The solutions were filtered through a micro-porous membrane (pore size,  
125 0.45 μm; diameter, 13 mm) before analysis and the WSIs (Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>  
126 and K<sup>+</sup>) in the treated filtrates were analyzed by Ion Chromatography (IC, WAYEE IC6200) which  
127 has been described in detail by our previous study (P. Liu et al., 2016). A quarter of each filter was  
128 cut into fragments and digested with 5 mL 65 % HNO<sub>3</sub> and 2 mL 30 % H<sub>2</sub>O<sub>2</sub> (Li et al., 2015) by a  
129 microwave digestion system (SINEO, MASTER-40). The digestion solution was diluted to 25 mL



130 with ultrapure water to insure the solution acidity below 10 % and the trace elements (Al, Mn, Fe,  
 131 Cu, Zn, As, Se, Sr, Tl and Pb) in the diluted solution were analyzed by a triple-quadrupole  
 132 inductively coupled plasma mass spectrometry (ICP-MS/MS, Agilent 8800). The standard  
 133 reference material (GBW07427) was also digested in the same way as the samples and the  
 134 recoveries of the trace elements were within the allowable ranges of the certified values ( $100 \pm$   
 135 15 %). Another quarter of each filter was analyzed by a DRI thermal optical carbon analyzer  
 136 (DRI-2001A) for carbon components (OC and EC). In addition, the PTFE filters were only used  
 137 for analyzing the WSIs (P. Liu et al., 2016).

### 138 2.3 Chemical mass closure

139 Chemical mass closure (CMC) method was adopted by considering secondary inorganic aerosols  
 140 (SIA, the sum of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{NH}_4^+$ ), sea salt & coal combustion (derived from  $\text{Cl}^-$  and  $\text{Na}^+$ ),  
 141 biomass burning (characterized by  $\text{K}^+$ ), mineral dust, EC, primary organic carbon (POC),  
 142 secondary organic carbon (SOC) and trace element oxide (TEO) (Hsu et al., 2010b; Zhang et al.,  
 143 2013; Mantas et al., 2014; Tian et al., 2014; Kong et al., 2015).

144 Atmospheric  $\text{Na}^+$  and  $\text{Cl}^-$  were considered to be from both sea salt and coal combustion during  
 145 winter in the North China (Brewer, 1975; van Eyk et al., 2011; Bläsing and Müller, 2012; Yu et al.,  
 146 2013; Wu et al., 2014; He et al., 2015; P. Liu et al., 2016), and their mass concentrations followed  
 147 the four equations:

$$148 \quad [\text{Cl}_{cc}^-] + [\text{Cl}_{ss}^-] = [\text{Cl}^-] \quad (1)$$

$$149 \quad [\text{Na}_{cc}^+] + [\text{Na}_{ss}^+] = [\text{Na}^+] \quad (2)$$

$$150 \quad \frac{[\text{Cl}_{cc}^-]/35.5}{[\text{Na}_{cc}^+]/23} = 1.4 \quad (3)$$



$$151 \quad \frac{[Cl_{ss}^-]/35.5}{[Na_{ss}^+]/23} = 1.18 \quad (4)$$

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

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

$$163 \quad [Mineral\ dust] = \frac{[Al]}{0.07} \quad (5)$$

164 POC and SOC were calculated by the EC-tracer OC/EC method (Cheng et al., 2011; Zhao et al.,  
 165 2013b; G. J. Zheng et al., 2015; Cui et al., 2015) as follows:

$$166 \quad [POC] = [EC] \times \left( \frac{[OC]}{[EC]} \right)_{pri} = K[EC] + M \quad (6)$$

$$167 \quad [SOC] = [OC] - [POC] \quad (7)$$

168 The values of  $K$  and  $M$  are estimated by linear regression analysis using the data pairs with the  
 169 lowest 10 % percentile of ambient OC/EC ratios.

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



$$172 \quad EF = \frac{([Element]/[Al])_{aerosol}}{([Element]/[Al])_{crust}} \quad (8)$$

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

$$178 \quad [TEO] = 1.3 \times ([Cu] + [Zn] + [Pb] + [As] + [Se] + [Tl] + 0.5 \times [Mn]) \quad (9)$$

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

#### 183 2.4 Meteorological, trace gases and back trajectory

184 Both the meteorological data, including wind speed, wind direction, relative humidity (RH),  
185 temperature, barometric pressure and air quality index (AQI) of  $PM_{2.5}$ ,  $SO_2$ ,  $NO_2$ , CO,  $O_3$  at BJ,  
186 BD and WD were obtained from Beijing urban ecosystem research station in RCEES, CAS  
187 (<http://www.bjurban.rcees.cas.cn/>), environmental protection bureau of Baoding City  
188 (<http://bdhb.gov.cn/>) and environmental monitoring station of Wangdu County  
189 (<http://www.wdx.gov.cn/>), respectively. The meteorological data at BJ and BD is shown in Fig. 3  
190 and the average concentrations of  $SO_2$  and  $NO_2$  at BJ, BD and WD are listed in Table 2 during the  
191 sampling period in the winter of 2015, which would be discussed in section 3.2 and 3.3.

192 The air mass backward trajectories were calculated for 24 h through the National Oceanic and  
193 Atmospheric Administration (NOAA) Hybrid Single-Particle Lagrangian Integrated Trajectory



194 Version 4 model (HYSPLIT 4 model) with National Centers for Environmental Prediction's  
195 (NCEP) global data. The backward trajectories arriving at 500 m above sampling position were  
196 computed at 0:00 h, 6:00 h, 12:00 h and 18:00 h (UTC) for each sampling day, respectively. A  
197 K-means cluster method was then used for classifying the trajectories into several different  
198 clusters and suitable clusters were selected for further analysis.

### 199 **3 Results and discussion**

#### 200 **3.1 Comparison of atmospheric WSIs between BJ and DBT**

201 The daily variations of atmospheric WSIs during the sampling periods at the two sampling sites of  
202 BJ and DBT are shown in Fig. 4. It is evident that the variations of the WSIs between the two  
203 sampling sites of BJ and DBT exhibited similar trend, but the mass concentrations of the WSIs  
204 were remarkably greater at DBT than at BJ during the two winter seasons. As listed in Table 1, the  
205 average concentrations of the typical WSIs were a factor of 1.5-2.0 greater at DBT than at BJ  
206 during the two winter seasons, whereas they were approximately the same at the two sampling  
207 sites during the two spring seasons. To clearly reveal the differences, the daily D-values (the  
208 concentrations of WSIs at DBT minus those at BJ) of several typical WSIs as well as the total  
209 WSIs between DBT and BJ are individually illustrated in Fig. 5. With only the exception for Ca<sup>2+</sup>  
210 (typical mineral dust component), the D-values of NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup> between DBT and BJ  
211 exhibited obviously positive values during the most sampling days in the two winter seasons,  
212 implying that the sources related to mineral dust could be excluded for explaining the obviously  
213 higher concentrations of the WSIs at DBT than at BJ. The sampling site of DBT is adjacent to  
214 Baoding city where the AQI during the winter always ranked the top three among Chinese cities in  
215 recent years (<http://113.108.142.147:20035/emcpublish/>), and hence the relatively greater



216 concentrations of the WSIs at DBT might be due to the regional pollution. However, the emissions  
217 of pollutants from industries, power plants and vehicles are usually relatively stable, which could  
218 not account for the remarkable differences of the D-values between the winters and the springs  
219 (Fig. 5). If the relatively high concentrations of the WSIs at DBT during the winter were ascribed  
220 to the regional pollution, there would be additional strong sources for them in the area of Baoding.  
221 To explore whether the regional pollution was responsible for the relatively high concentrations of  
222 the WSIs at DBT in winter, the various species in PM<sub>2.5</sub> collected simultaneously at DBT and its  
223 neighbor cities of WD, BD and BJ in the winter of 2015 were further investigated in the following  
224 section.

### 225 **3.2 Daily variations of the species in PM<sub>2.5</sub> at the four sampling sites**

226 The daily variations of the species in PM<sub>2.5</sub> at the four sampling sites also exhibited similar  
227 fluctuation trends (Fig. 6), implying that the regional meteorological conditions which are  
228 dominant factors for the dispersion and accumulation of atmospheric pollutants (Xu et al., 2011;  
229 Tao et al., 2012; Sun et al., 2013; Chen et al., 2015; Gao et al., 2016) were similar (Fig. 3) during  
230 the sampling period. However, there was obvious difference in the concentrations of OC, EC,  
231 NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup> and K<sup>+</sup> among the four sampling sites, ranked in order as BJ < WD < BD <  
232 DBT. As listed in Table 2, the average concentration of the total species at DBT was about a factor  
233 of 2.7, 1.8 and 1.4 higher than those at BJ, WD and BD, respectively. The largest levels of the key  
234 species in PM<sub>2.5</sub> at DBT among the four sampling sites implied that the pollutants at the rural site  
235 were not through the air parcel transportation from its neighbor cities but mainly ascribed to the  
236 local emissions or formation. Vehicles and industries could be rationally excluded for explaining  
237 the largest levels of the key species in PM<sub>2.5</sub> at DBT, because these sources are very sparse in the



238 rural area around DBT (See section 3.4). Compared with the cities, the distinct source for  
239 atmospheric pollutants at DBT in winter is the residential coal combustion which is prevalingly  
240 used for heating and cooking in rural areas of the Northern China. The emissions of various  
241 pollutants from residential coal combustion were very serious due to lack of any control measures,  
242 strong smoke could be seen in the chimney of the residential coal stoves. The emission factors of  
243 OC and EC from residential coal combustion were reported to be 0.47-7.82 g kg<sup>-1</sup> coal and  
244 0.028-2.75 g kg<sup>-1</sup> coal, respectively (Chen et al., 2005; Zhang et al., 2008). The emission factors of  
245 various pollutants from a typical residential coal stove fueled with raw bituminous coal were also  
246 investigated in our group (Du et al., 2016; Liu et al., 2017) according to farmers' customary uses  
247 of coal stoves under the alternation cycles of flaming and smoldering. The emission factors of OC  
248 and EC under the entire combustion process could achieve to be 10.99 ± 0.95 g kg<sup>-1</sup> coal and 0.84  
249 ± 0.06 g kg<sup>-1</sup> coal, respectively (Table 3). Considering the high density of farmers in the rural area,  
250 the largest levels of atmospheric OC and EC at DBT could be rationally ascribed to residential  
251 coal combustion. However, the proportion of the WSIs from residential coal combustion (Fig. 7a)  
252 were extremely low with respect to that of the atmosphere. Therefore, the largest levels of the key  
253 WSIs in PM<sub>2.5</sub> at DBT were suspected to the secondary formation via the heterogeneous or  
254 multiphase reactions which might be accelerated by the OC and EC (Han et al., 2013; Zhao et al.,  
255 2016) emitted from residential coal combustion.

256 Although the three sampling sites of DBT, WD and BD are closely adjacent, the lowest  
257 concentrations of the key species in PM<sub>2.5</sub> were observed at WD, which was probably ascribed to  
258 the replacement of coal with natural gas for the central heating in the county of WD (a main pipe  
259 of natural gas is just across the county), e.g., the average concentration of NO<sub>2</sub> was higher at WD



260 than at BD, whereas the average concentration of SO<sub>2</sub> was on the contrary (Table 2).  
261 The city of BD and the county of WD are fully surrounded by high density of countryside,  
262 whereas the city of BJ is only neighbored with high density of countryside in the  
263 south-southeast-southwest directions, and thus the residential coal combustion was also suspected  
264 to be responsible for the remarkably higher concentrations of the key species in PM<sub>2.5</sub> at BD and  
265 WD than at BJ. To confirm the above assumptions, the chemical composition and source  
266 characteristics of the species in PM<sub>2.5</sub> were further analyzed in the following section.

### 267 3.3 Chemical composition of PM<sub>2.5</sub> at the four sampling sites

268 The average mass proportions of the species in PM<sub>2.5</sub> during the sampling period at the four  
269 sampling sites are illustrated in Fig. 7b. OC, EC, NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> were found to be the  
270 principal species, accounting for about 82 %-88 % of the total species in PM<sub>2.5</sub> at each sampling  
271 site, which were in line with previous studies (Zhao et al., 2013a; X. J. Zhao et al., 2013; Tian et  
272 al., 2014; Huang et al., 2014). As for the proportions of individual species, there were obvious  
273 differences between the sampling site of BJ and the sampling sites of BD, WD and DBT. The  
274 average mass proportions of OC and EC at BD, WD and DBT were very close, accounting for  
275 about 45.7 %-47.1 % and 9.0 %-10.4 % of the total species in PM<sub>2.5</sub>, respectively, which were  
276 about 8 % for OC and 2 % for EC greater than those at BJ. In contrast to OC and EC, the average  
277 mass proportions of NO<sub>3</sub><sup>-</sup> (10.1 %-10.8 %) and SO<sub>4</sub><sup>2-</sup> (11.2 %-11.7 %) at BD, WD and DBT were  
278 about 5 % and 3 % less than those (15.1 % for NO<sub>3</sub><sup>-</sup> and 14.0 % for SO<sub>4</sub><sup>2-</sup>) at BJ, respectively. The  
279 obvious differences of the mass proportions of OC, EC, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> between the sampling site  
280 of BJ and the sampling sites of BD, WD and DBT indicated that the sources for the principal  
281 species at BJ were different from the other three sampling sites. The mass proportions of OC, EC,



282  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  at BD and WD were very close to those at DBT, implying that residential coal  
283 combustion might also be the dominant source for the species in  $\text{PM}_{2.5}$  at BD and WD. Residential  
284 sector (dominated by residential coal combustion) in the region of BTH during winter has been  
285 recognized as the dominant source for atmospheric OC and EC, which was estimated to contribute  
286 85% and 65% of primary OC and EC emissions, respectively (J. Liu et al., 2016). Because the  
287 sampling sites of DBT, BD and WD are located in or fully surrounded by high density of  
288 countryside, the contribution of residential coal combustion to atmospheric OC and EC at DBT,  
289 BD and WD must evidently exceed the regional values estimated by J. Liu et al. (2016).

290 Although the mass proportions of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  were evidently lower at BD, WD and DBT than  
291 at BJ, the average mass concentrations of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  were on the contrary (Table 2).  
292 Atmospheric  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  are mainly from secondary formation via heterogeneous, multiphase  
293 or gas-phase reactions which are depended on the concentrations of their precursors ( $\text{NO}_2$  and  $\text{SO}_2$ )  
294 and OH radicals, the surface characteristics and areas of particles, and RH (Ravishankara, 1997;  
295 Wang et al., 2013; Quan et al., 2014; Nie et al., 2014; He et al., 2014; Yang et al., 2015; B. Zheng  
296 et al., 2015). The remarkably higher concentrations of  $\text{NO}_2$ ,  $\text{SO}_2$  and  $\text{PM}_{2.5}$  at BD, WD and DBT  
297 (Liu et al., 2015) than at BJ (Table 2) favored secondary formation of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ , resulting in  
298 the relatively high concentrations of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ .

299 As shown in Fig. 8, the serious pollution episodes at BJ usually occurred during the periods with  
300 the air parcel from the southwest-south directions where farmers with high density reside, and thus  
301 residential coal combustion might also make evident contribution to atmospheric pollutants at BJ.  
302 Because the species in  $\text{PM}_{2.5}$  at BJ during the serious pollution episodes accounted for very large  
303 weight of their average concentrations, the proportions of the species in  $\text{PM}_{2.5}$  were dominated by



304 the serious pollution events. The highest  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  proportions and the lowest OC and EC  
305 proportions at BJ among the four sampling sites might be partly ascribed to the conversions of  
306  $\text{NO}_2$  and  $\text{SO}_2$  to  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  during the air parcel transportation from the south-southwest  
307 directions. The contribution of the transportation to atmospheric OC and EC at BJ could be  
308 verified by the correlations between the OC/EC ratios and the  $\text{PM}_{2.5}$  levels (Fig. 9). The OC/EC  
309 ratios (about  $4.9 \pm 0.7$ ) at WD and DBT were almost independent of the  $\text{PM}_{2.5}$  levels, whereas the  
310 OC/EC ratios at BJ and BD remarkably decreased with increasing the  $\text{PM}_{2.5}$  levels and reached the  
311 almost same value (about  $4.8 \pm 0.5$ ) as those at WD and DBT when the concentrations of  $\text{PM}_{2.5}$   
312 were above  $150 \mu\text{g m}^{-3}$  (the serious pollution events). Because there were relatively sparse  
313 emissions from vehicles and industries at WD and DBT, the almost constant of OC/EC ratios  
314 under the different levels of  $\text{PM}_{2.5}$  at WD and DBT further revealed that atmospheric OC and EC  
315 were dominated by the local residential coal combustion. The almost same OC/EC ratios at the  
316 four sampling sites with the concentrations of  $\text{PM}_{2.5}$  greater than  $150 \mu\text{g m}^{-3}$  indicated that the  
317 residential coal combustion also made dominant contribution to atmospheric OC and EC in the  
318 two cities during the severe pollution period. Our previous study (C. Liu et al., 2016) also found  
319 that the contribution from residential coal combustion to atmospheric VOCs increased from 23 %  
320 to 33 % with increasing pollution levels in Beijing.

321 It should be mentioned that the OC/EC ratios observed at DBT and WD were about a factor of 2.7  
322 less than that (13.1) of the emission from the residential coal combustion, whereas at BJ and BD  
323 were too high to be explained by direct emissions from diesel (0.4-0.8) and gasoline (3.1) vehicles  
324 (Shah et al., 2004; Geller et al., 2006). The OC emitted from the residential coal combustion might  
325 be easily degraded or volatilized in the atmosphere, resulting in the relatively low OC/EC ratios



326 observed at DBT and WD. In China, aromatic compounds as typical pollutants from vehicle  
327 emissions are very reactive to make contribution to secondary organic aerosols (SOA) (Zhang et  
328 al., 2017), which was suspected to make evident contribution to the OC/EC ratios at BJ and BD  
329 when the atmospheric EC concentrations were relatively low. For example, the extremely high  
330 OC/EC ratios ( $> 6.0$ ) at BJ and BD only occurred when the atmospheric EC concentrations were  
331 less than  $3.2 \mu\text{g m}^{-3}$  at BJ and  $5.4 \mu\text{g m}^{-3}$  at BD. Because the atmospheric EC concentrations at BJ  
332 and BD were about a factor of 4-6 greater during the serious pollution events than during the  
333 slight pollution events, the effect of SOA formation on the OC/EC ratios would become less  
334 during the serious pollution events if the SOA formation rate kept constant.

### 335 **3.4 Correlations among the species in $\text{PM}_{2.5}$**

336 The correlations among the WSIs, OC and EC in  $\text{PM}_{2.5}$  at the four sampling sites are listed in  
337 [Table 4](#). The number of the species involved in significant correlations evidently increased from  
338 the countryside to the cities and was 18, 28, 30 and 36 at DBT, WD, BD and BJ, respectively. The  
339 significant correlations among the species could be classified as three types: 1) associated with OC  
340 and EC; 2) associated with  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ; and 3) associated with  $\text{K}^+$ . Three types of significant  
341 correlations at DBT were independent of each other, whereas they were involved in interrelation  
342 more and more from WD to BJ. The independence for the three types of significant correlations at  
343 DBT further confirmed that residential coal combustion was preferentially dominant source for  
344 atmospheric OC and EC. The significant correlations among OC, EC,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$  and  $\text{Cl}^-$  at DBT  
345 indicated that the OC and EC emitted from the residential coal combustion could quickly  
346 accelerate secondary formation of  $\text{NO}_3^-$ ,  $\text{NH}_4^+$  and  $\text{Cl}^-$  via heterogeneous or multiphase reactions  
347 of  $\text{NO}_x$ ,  $\text{NH}_3$  and  $\text{HCl}$  which have been verified to be emitted from the residential coal combustion



348 (Wang et al., 2005; Shapiro et al., 2007; Blasing and Müller, 2010; Meng et al., 2011; Zhang et al.,  
349 2013; Gao et al., 2015; Li et al., 2016a; Huang et al., 2016). The interrelation for the three types of  
350 significant correlations at WD, BD and BJ implied that complex sources including local emissions  
351 and regional transportation were dominant for atmospheric species in the cities. The species  
352 associated with  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  from construction and road dust (Liang et al., 2016) as well as the  
353 species associated with  $\text{K}^+$  from biomass (municipal solid waste) burning (Gao et al., 2011; J. Li et  
354 al., 2014; Yao et al., 2016) in the cities would accumulate under stagnant air conditions at the earth  
355 surface, meanwhile the OC and EC concentrations could also increase due to the air parcel  
356 transportation with abundant OC and EC in the upper layer from the south-southwest directions  
357 (Fig. 8). It is interesting to note that the significant correlations among OC, EC,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$  and  
358  $\text{Cl}^-$  were found at the four sampling sites, whereas the significant correlation between OC (or EC)  
359 and  $\text{SO}_4^{2-}$  was only found at BJ. Because the sampling sites of DBT, WD and BD are close to the  
360 source of OC and EC from the residential coal combustion, the significant correlations among OC,  
361 EC,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$  and  $\text{Cl}^-$  but the insignificant correlation between OC (or EC) and  $\text{SO}_4^{2-}$  implied  
362 that the formation rate of  $\text{SO}_4^{2-}$  via heterogeneous or multiphase reactions might be relatively  
363 slower than those of  $\text{NO}_3^-$ ,  $\text{NH}_4^+$  and  $\text{Cl}^-$ . The OC, EC and  $\text{SO}_2$  emitted from the residential coal  
364 combustion experienced the relatively long period of excursion to be transported to Beijing,  
365 resulting in the significant correlation between OC (or EC) and  $\text{SO}_4^{2-}$  at BJ.

366 As listed in Table 5, the pronounced correlations for [As] vs. [Se] and [Cu] vs. [Zn] at the four  
367 sampling sites indicated that the two pairs of elements were from the common sources. Based on  
368 the remarkable elevations of As and Se near a coal-fired power plant with respect to the  
369 background site, Jayasekher (2009) pointed out that their significant correlation can be used as the



370 tracer for coal combustion. Because Cu and Zn have been found to be mainly released from the  
371 additives of vehicle lubricating oils, brake and tire wear during transportation activities (Yu et al.,  
372 2013; Zhang et al., 2013; Tan et al., 2016), their significant correlation has been used as the tracer  
373 for vehicle emissions. Both coal combustion and vehicle emissions could make contribution to  
374 atmospheric Pb (Zhang et al., 2013; Gao et al., 2016), and thus the correlations for [Pb] vs.  
375 [Cu+Zn] and [Pb] vs. [As+Se] could reflect their local dominant sources. As shown in Fig. 10, the  
376 significant correlation between [Pb] and [Cu+Zn] but no correlation between [Pb] and [As+Se]  
377 were found at BJ, whereas the correlations at the rural site of DBT were on the contrary, indicating  
378 that atmospheric Pb, Cu and Zn at BJ were mainly related to the vehicle emissions and  
379 atmospheric Pb, As and Se at DBT were dominated by residential coal combustion. Because the  
380 sampling sites of BD and WD were affected by both vehicle emissions and residential coal  
381 combustion, the significant correlations between [Pb] and [Cu+Zn] as well as [Pb] and [As+Se]  
382 were found at the two sampling sites. Although there was no correlation between [Pb] and [As+Se]  
383 at BJ, the contribution of residential coal combustion to atmospheric PM<sub>2.5</sub> in the city of BJ could  
384 not be excluded because the trace elements from coal combustion are mainly present in relatively  
385 large particles (0.8-2.5 μm) which might quickly deposit near their sources (Wang et al., 2008).

### 386 **3.5 Source apportionment of PM<sub>2.5</sub> at the four sampling sites**

387 The source characteristics of PM<sub>2.5</sub> at the four sampling sites were analyzed by the CMC method  
388 which has been described in detail in section 2.3. The average proportions of the species from  
389 different sources in PM<sub>2.5</sub> during the sampling period at the four sampling sites are comparatively  
390 shown in Fig. 11. It is evident that secondary aerosols (SIA + SOC) accounted for the largest  
391 proportion (about 32-41 %) in PM<sub>2.5</sub>, followed by POC (about 24-28 %), EC (about 6-8 %),



392 mineral dust (about 2-8 %) and  $\text{Cl}^-_{\text{cc}}$  (about 2-5 %) at the four sampling sites. The proportion of  
393 mineral dust was the highest at BJ and the lowest at DBT among the four sampling sites, whereas  
394 the proportion of  $\text{Cl}^-_{\text{cc}}$  was on the contrary. Because the concentrations of the mineral dust  
395 compounds were much higher under stagnant weather condition than under clean days at BJ, the  
396 remarkably high proportion of mineral dust at BJ was mainly ascribed to the emissions from road  
397 dust and construction (Liang et al., 2016) during the sampling period. The obviously high  
398 proportion of  $\text{Cl}^-_{\text{cc}}$  at DBT was ascribed to the emission from residential coal combustion (Shen et  
399 al., 2016). In addition, the proportions of TEO,  $\text{K}^+_{\text{bb}}$  and  $\text{Cl}^-_{\text{ss}}$  were less than about 2 %, which  
400 were insignificant to the sources of  $\text{PM}_{2.5}$  at the four sampling sites during the sampling period.  
401 Atmospheric Primary Organic Matters (POM) and  $\text{Cl}^-_{\text{cc}}$  at the four sampling sites could be  
402 estimated based on  $\text{POM} \approx \text{POC} \times 1.6$  (Cheung et al., 2005; Hsu et al., 2010b; Han et al., 2015)  
403 and the formulas (1)-(4), respectively. The sum of POM, EC and  $\text{Cl}^-_{\text{cc}}$  at DBT was assumed to be  
404 solely from residential coal combustion, accounting for about 58% in  $\text{PM}_{2.5}$  (Fig. 12). Assuming  
405 that the ratio of  $\text{Cl}^-_{\text{cc}}$  to the sum of POM, EC and  $\text{Cl}^-_{\text{cc}}$  was constant for coal combustion at the four  
406 sampling sites, the primary contribution of coal combustion to atmospheric  $\text{PM}_{2.5}$  at BJ, BD and  
407 WD could be estimated to be 32 %, 49 % and 43 % (Fig. 12), respectively. The annual residential  
408 coal consumption mainly focused on the four months in winter, accounting for about 11 % of the  
409 total coal consumption in the region of BTH. Because the emission factor of  $\text{PM}_{2.5}$  from  
410 residential coal combustion (about 1054-12910  $\text{mg kg}^{-1}$ ) was about 1-3 orders of magnitude  
411 greater than those from industry boilers or coal power plants (about 16-100  $\text{mg kg}^{-1}$ ) (Chen et al.,  
412 2005; Zhang et al., 2008), the estimated proportions of the contribution of coal combustion to  
413 atmospheric  $\text{PM}_{2.5}$  at the four sampling sites during the winter were mainly ascribed to residential



414 coal combustion. If only the primary  $PM_{2.5}$  was considered, the contribution of residential coal  
415 combustion to the primary  $PM_{2.5}$  at BJ would achieve to be about 59 % which was in line with the  
416 value of 57 % estimated by J. Liu et al. (2016) for the winter of 2010 in Beijing.

#### 417 **4 Conclusions**

418 Based on the comprehensive analysis of the levels, composition characteristics, the correlations of  
419 the key species in  $PM_{2.5}$  and the back trajectories, residential coal combustion in the North China  
420 during winter was found not only to be the dominant source for atmospheric OC, EC, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>,  
421 SO<sub>4</sub><sup>2-</sup> and NH<sub>4</sub><sup>+</sup> in rural areas but also to make evident contribution to the species in cities.  
422 According to the CMC method, the contributions of the primary particle emission from residential  
423 coal combustion to atmospheric  $PM_{2.5}$  at BJ, BD, WD and DBT during winter were estimated to  
424 be 32 %, 49 %, 43 % and 58 %, respectively. Therefore, strict control measures should be  
425 implemented for the emissions from residential coal combustion to mitigate the currently serious  
426  $PM_{2.5}$  pollution during the winter in the North China.

#### 427 **Author contribution**

428 **Y. J. Mu** designed the experiments and prepared the manuscript. **P. F. Liu** carried out the  
429 experiments and prepared the manuscript. **C. Y. Xue** and **C. L. Zhang** carried out the experiments.  
430 **J. F. Liu**, **Y. Y. Zhang**, **D. Tian** and **C. Ye** were involved in part of the work. **H. X. Zhang**  
431 provided the meteorological data and trace gases in Beijing. **J. Guan** provided the meteorological  
432 data and trace gases in Baoding and Wangdu.

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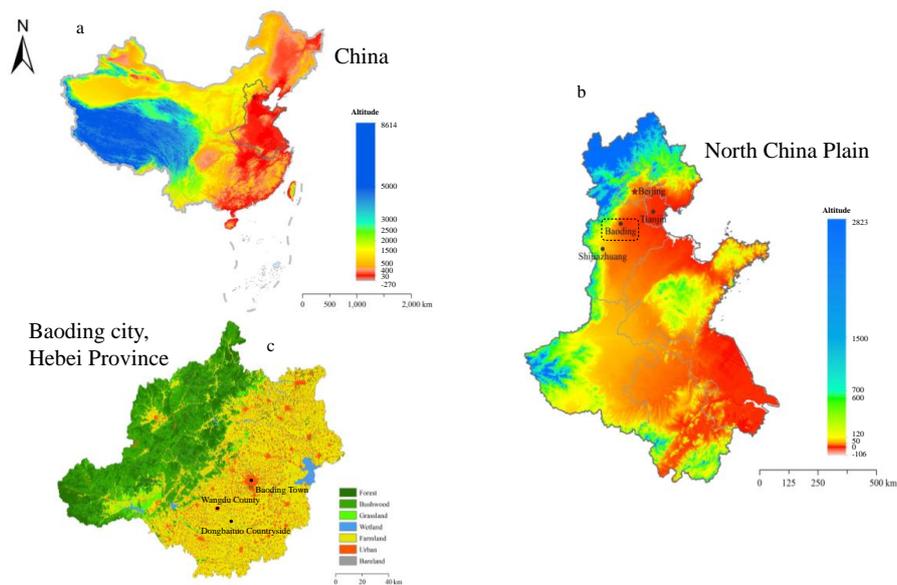
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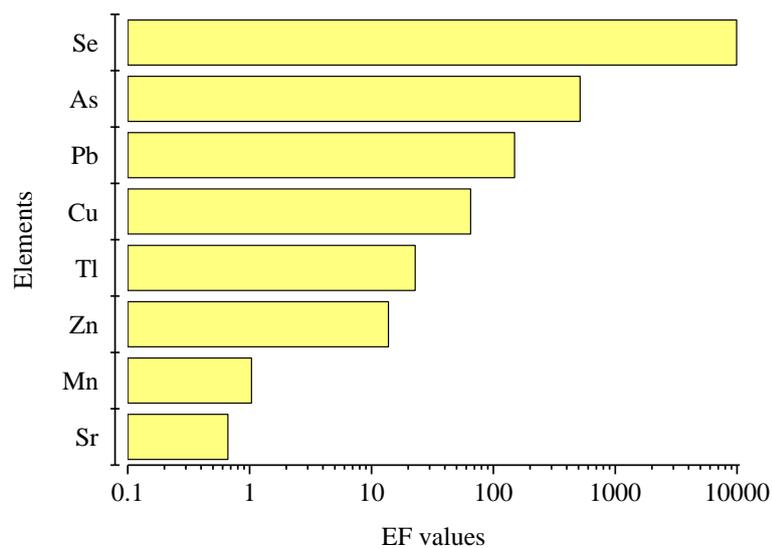
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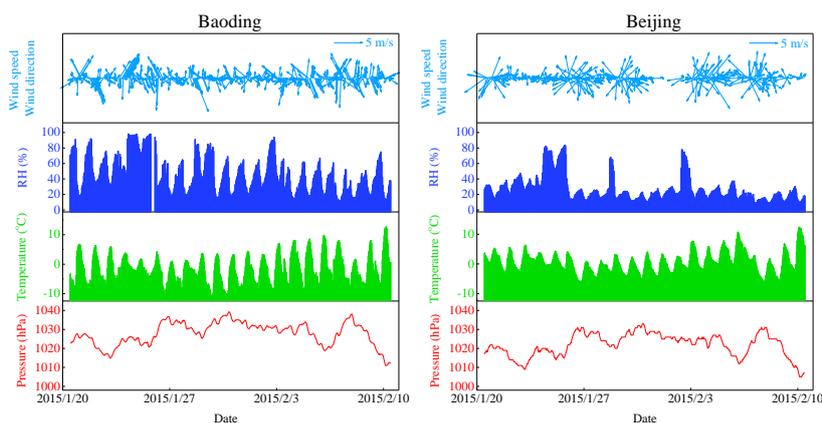
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**Figure 1.** China (a), the North China Plain (b) and Baoding city in Hebei Province (c). The locations of sampling sites (BJ, BD, WD and DBT) as well as Tianjin municipality and Shijiazhuang as provincial capital of Hebei are marked.



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**Figure 2.** Enrichment factor values for trace elements in PM<sub>2.5</sub>.

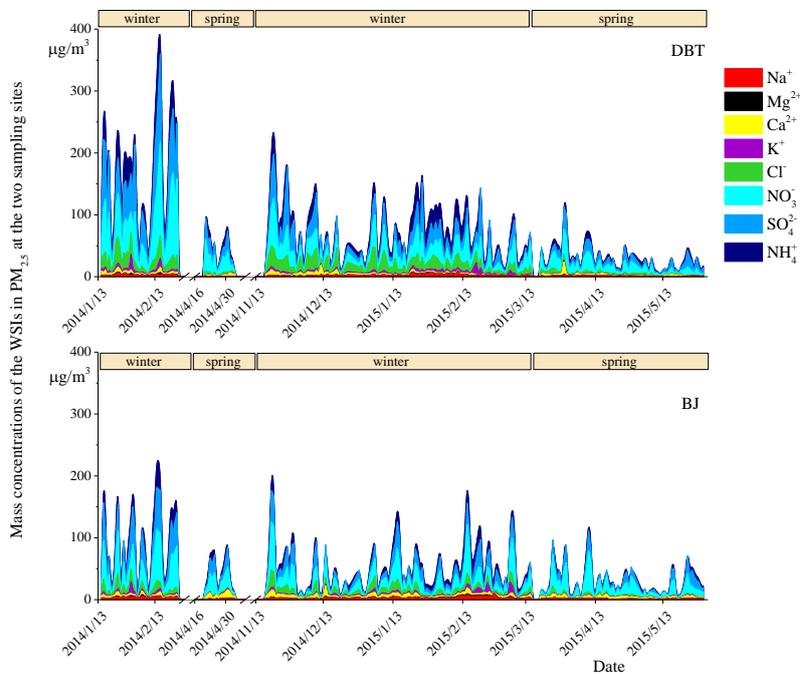


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**Figure 3.** The wind speed, wind direction, RH, temperature and barometric pressure at BD and BJ during the sampling period in the winter of 2015.

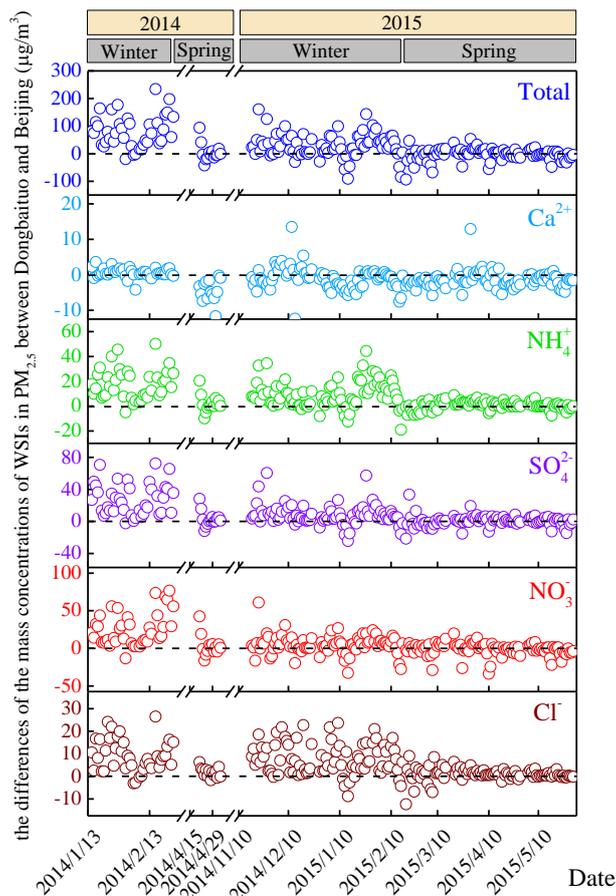


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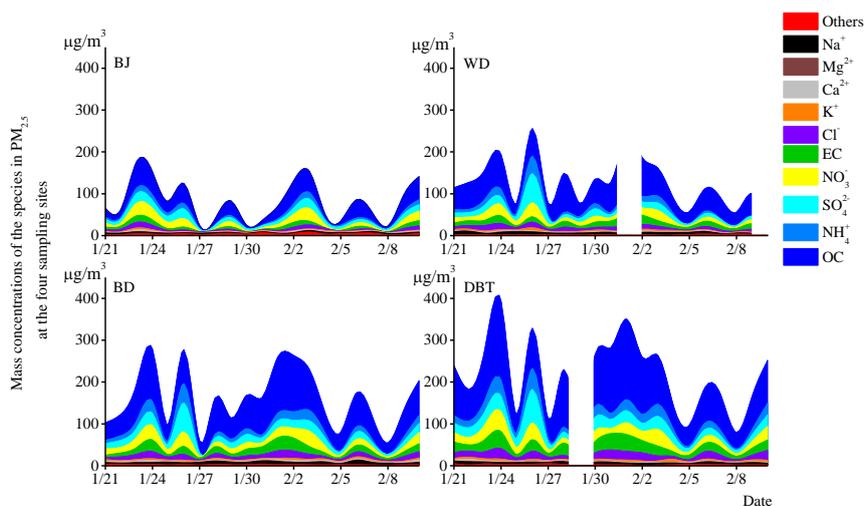
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**Figure 4.** The mass concentrations of the WSIs in PM<sub>2.5</sub> at DBT and BJ during the sampling period in the winters and springs of 2014-2015.



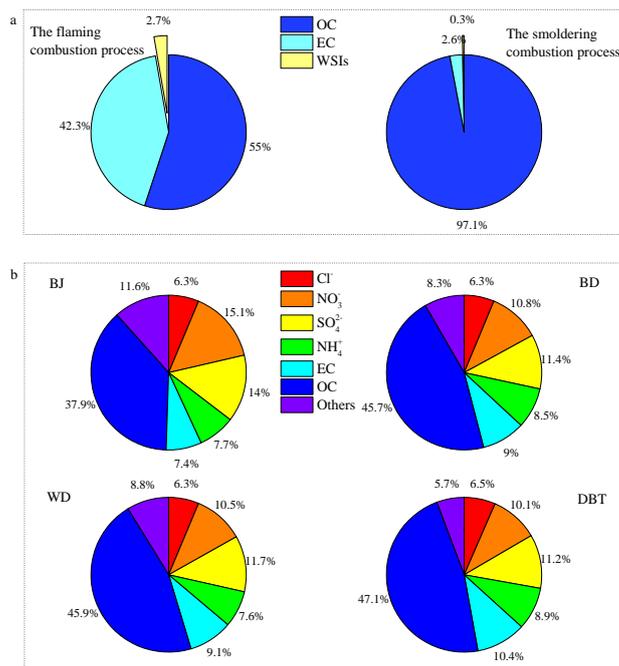
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**Figure 5.** The D-values of the mass concentrations of WSIs in  $PM_{2.5}$  between DBT and BJ during the sampling period in the winters and springs of 2014-2015.



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**Figure 6.** Daily variation of the species in PM<sub>2.5</sub> at the four sampling sites during the sampling period in the winter of 2015.

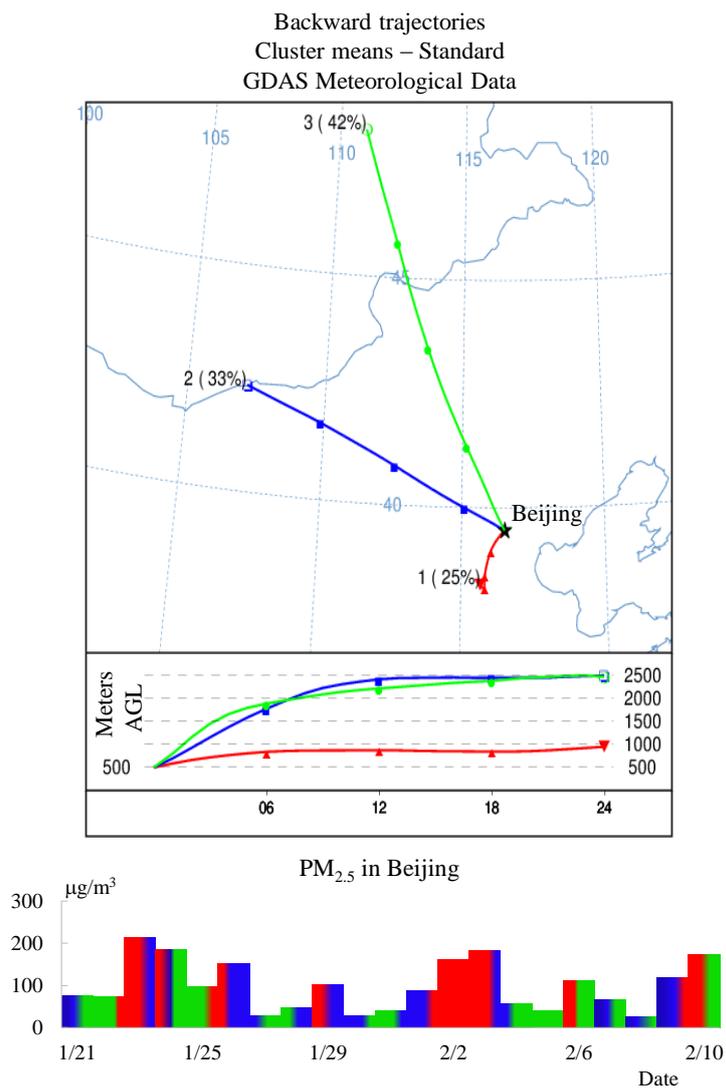


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**Figure 7.** The mass proportions of OC, EC and WSIs from residential coal combustion under the flaming and smoldering combustion processes (a), and the average mass proportions of the typical

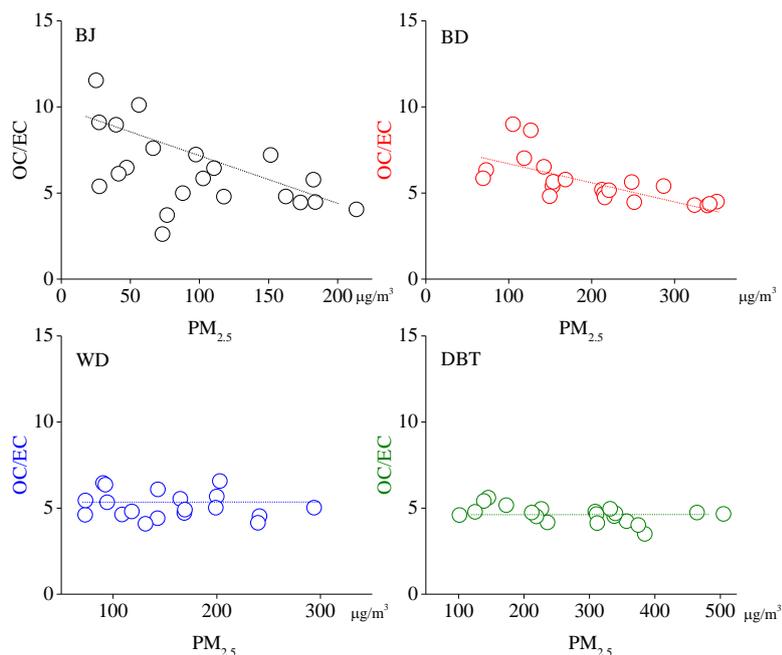


790 species in  $PM_{2.5}$  at the four sampling sites during the sampling period in the winter of 2015 (b).



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**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.

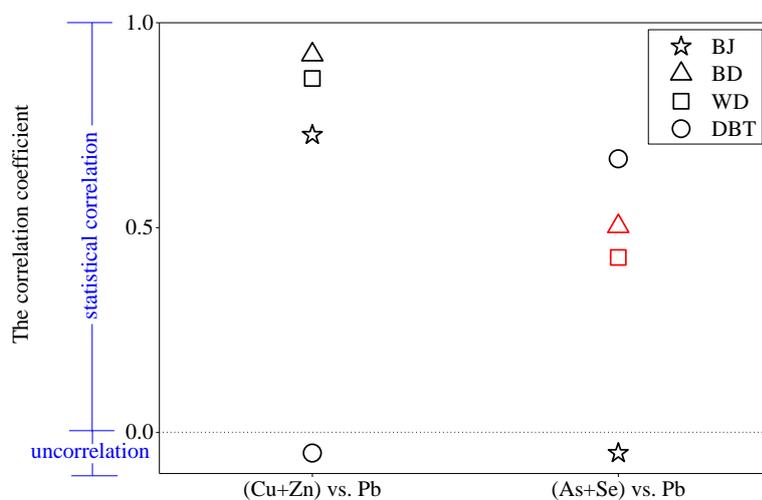


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**Figure 9.** The correlations between the OC/EC ratios and the  $PM_{2.5}$  concentrations at the four sampling sites during the sampling period in the winter of 2015.



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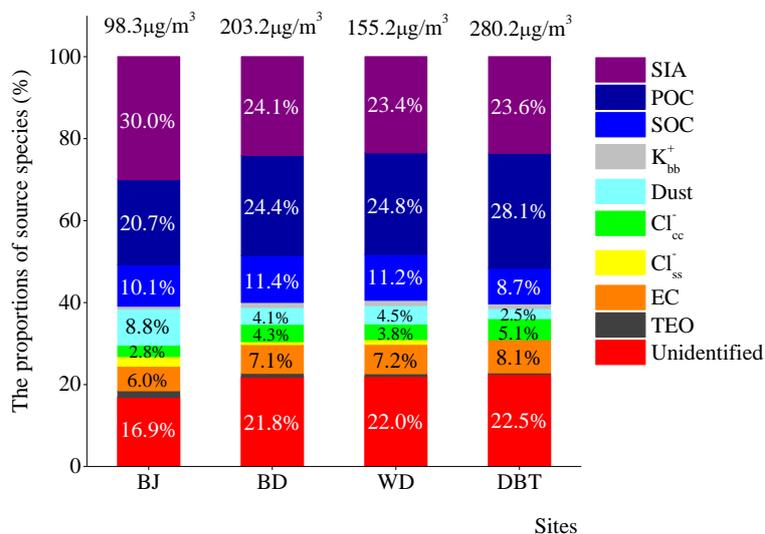
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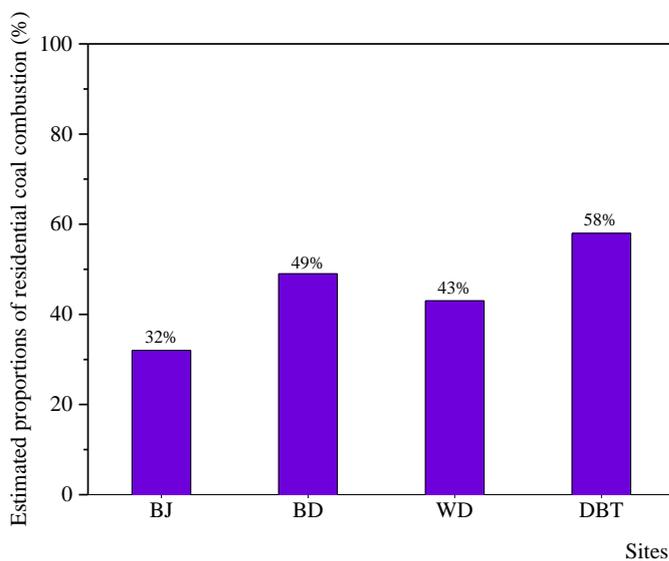
**Figure 10.** The statistical correlations for  $[Cu+Zn]$  vs.  $[Pb]$  and  $[As+Se]$  vs.  $[Pb]$  in  $PM_{2.5}$  at the four sampling sites during the sampling period in the winter of 2015. The uncorrelated results are



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



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 804 **Figure 11.** The proportions of source species under the constructed chemical mass closures for  
 805 PM<sub>2.5</sub> at the four sampling sites during the sampling period in the winter of 2015. Average mass  
 806 concentrations of PM<sub>2.5</sub> at each sampling site, including all of source species and unidentified  
 807 fractions, are also marked at the top of bar charts.



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809 **Figure 12.** The estimated contributions of coal combustion to the PM<sub>2.5</sub> at the four sampling sites  
 810 during the sampling period in the winter of 2015.

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812 **Table 1.** The average mass concentrations of WSIs in PM<sub>2.5</sub> at DBT and BJ during the sampling  
 813 period in the winters and springs of 2014-2015 ( $\mu\text{g m}^{-3}$ ).

| WSIs                          | spring      |             | winter       |             |
|-------------------------------|-------------|-------------|--------------|-------------|
|                               | DBT         | BJ          | DBT          | BJ          |
| Na <sup>+</sup>               | 1.0 ± 0.5   | 1.4 ± 0.5   | 2.4 ± 1.3    | 3.1 ± 1.4   |
| Mg <sup>2+</sup>              | 0.2 ± 0.2   | 0.3 ± 0.2   | 0.7 ± 0.5    | 0.8 ± 0.7   |
| Ca <sup>2+</sup>              | 1.7 ± 2.4   | 3.4 ± 2.5   | 2.6 ± 2.1    | 3.4 ± 2.3   |
| K <sup>+</sup>                | 0.5 ± 0.5   | 0.7 ± 0.4   | 3.2 ± 3.0    | 3.0 ± 6.0   |
| NH <sub>4</sub> <sup>+</sup>  | 6.1 ± 5.1   | 4.8 ± 4.7   | 23.1 ± 17.9  | 13.2 ± 11.6 |
| NO <sub>3</sub> <sup>-</sup>  | 12.5 ± 11.2 | 13.6 ± 13.2 | 28.4 ± 28.0  | 19.0 ± 20.0 |
| SO <sub>4</sub> <sup>2-</sup> | 10.5 ± 8.2  | 9.2 ± 8.6   | 29.0 ± 28.1  | 17.4 ± 16.5 |
| Cl <sup>-</sup>               | 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 |

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815 **Table 2.** The average mass concentrations (Mean ± SD) of PM<sub>2.5</sub> species, NO<sub>2</sub> and SO<sub>2</sub> at the four  
 816 sampling sites during the sampling period in the winter of 2015 ( $\mu\text{g m}^{-3}$ ).

| Species                       | BJ          | BD           | WD           | DBT          |
|-------------------------------|-------------|--------------|--------------|--------------|
| Na <sup>+</sup>               | 2.5 ± 0.7   | 4.8 ± 2.0    | 4.5 ± 1.7    | 4.3 ± 1.2    |
| Mg <sup>2+</sup>              | 0.3 ± 0.1   | 0.4 ± 0.1    | 0.3 ± 0.1    | 0.4 ± 0.2    |
| Ca <sup>2+</sup>              | 1.8 ± 0.9   | 2.6 ± 0.8    | 1.7 ± 0.6    | 2.0 ± 0.8    |
| K <sup>+</sup>                | 0.7 ± 0.8   | 2.5 ± 1.0    | 2.0 ± 1.4    | 3.1 ± 1.3    |
| NH <sub>4</sub> <sup>+</sup>  | 6.0 ± 5.0   | 13.3 ± 11.0  | 9.3 ± 9.5    | 18.7 ± 11.7  |
| NO <sub>3</sub> <sup>-</sup>  | 11.7 ± 10.1 | 16.6 ± 10.3  | 13.0 ± 8.2   | 21.0 ± 12.2  |
| SO <sub>4</sub> <sup>2-</sup> | 11.2 ± 6.5  | 18.1 ± 14.1  | 14.5 ± 14.5  | 24.1 ± 16.1  |
| Cl <sup>-</sup>               | 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 <sub>2</sub>               | 36.5 ± 17.4 | 60.4 ± 23.4  | 76.1 ± 19.2  | -            |
| SO <sub>2</sub>               | 63.9 ± 31.7 | 181.7 ± 62.4 | 101.3 ± 39.4 | -            |

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818 **Table 3.** The emission factors (Mean  $\pm$  SD) ( $\text{g kg}^{-1}$  coal) of OC and EC from residential coal  
 819 combustion during the flaming combustion process, the smoldering combustion process and the  
 820 entire combustion process.

| Emission factors | the flaming<br>combustion process | the smoldering<br>combustion process | the entire<br>combustion process |
|------------------|-----------------------------------|--------------------------------------|----------------------------------|
| OC               | $1.83 \pm 1.19$                   | $17.11 \pm 0.79$                     | $10.99 \pm 0.95$                 |
| EC               | $1.40 \pm 0.11$                   | $0.46 \pm 0.03$                      | $0.84 \pm 0.06$                  |

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822 **Table 4.** The correlations of several typical species in  $\text{PM}_{2.5}$  at the four sampling sites during the  
 823 sampling period in the winter of 2015.

|      |                    | BJ               |                  |              |               |                 |                    |                 |         |    |
|------|--------------------|------------------|------------------|--------------|---------------|-----------------|--------------------|-----------------|---------|----|
| n=21 |                    | $\text{Mg}^{2+}$ | $\text{Ca}^{2+}$ | $\text{K}^+$ | $\text{Cl}^-$ | $\text{NO}_3^-$ | $\text{SO}_4^{2-}$ | $\text{NH}_4^+$ | OC      | EC |
|      | $\text{Mg}^{2+}$   | 1                |                  |              |               |                 |                    |                 |         |    |
|      | $\text{Ca}^{2+}$   | 0.895**          | 1                |              |               |                 |                    |                 |         |    |
|      | $\text{K}^+$       | 0.634**          | 0.862**          | 1            |               |                 |                    |                 |         |    |
|      | $\text{Cl}^-$      | 0.856**          | 0.899**          | 0.791**      | 1             |                 |                    |                 |         |    |
|      | $\text{NO}_3^-$    | 0.803**          | 0.768**          | 0.637**      | 0.905**       | 1               |                    |                 |         |    |
|      | $\text{SO}_4^{2-}$ | 0.679**          | 0.660**          | 0.590**      | 0.804**       | 0.950**         | 1                  |                 |         |    |
|      | $\text{NH}_4^+$    | 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  |
|      |                    | BD               |                  |              |               |                 |                    |                 |         |    |
| n=21 |                    | $\text{Mg}^{2+}$ | $\text{Ca}^{2+}$ | $\text{K}^+$ | $\text{Cl}^-$ | $\text{NO}_3^-$ | $\text{SO}_4^{2-}$ | $\text{NH}_4^+$ | OC      | EC |
|      | $\text{Mg}^{2+}$   | 1                |                  |              |               |                 |                    |                 |         |    |
|      | $\text{Ca}^{2+}$   | 0.805**          | 1                |              |               |                 |                    |                 |         |    |
|      | $\text{K}^+$       | 0.697**          | 0.556**          | 1            |               |                 |                    |                 |         |    |
|      | $\text{Cl}^-$      | 0.714**          | 0.659**          | 0.789**      | 1             |                 |                    |                 |         |    |
|      | $\text{NO}_3^-$    | 0.554**          | 0.560**          | 0.675**      | 0.757**       | 1               |                    |                 |         |    |
|      | $\text{SO}_4^{2-}$ | 0.022            | 0.107            | 0.491*       | 0.499*        | 0.764**         | 1                  |                 |         |    |
|      | $\text{NH}_4^+$    | 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  |
|      |                    | WD               |                  |              |               |                 |                    |                 |         |    |
| n=19 |                    | $\text{Mg}^{2+}$ | $\text{Ca}^{2+}$ | $\text{K}^+$ | $\text{Cl}^-$ | $\text{NO}_3^-$ | $\text{SO}_4^{2-}$ | $\text{NH}_4^+$ | OC      | EC |
|      | $\text{Mg}^{2+}$   | 1                |                  |              |               |                 |                    |                 |         |    |
|      | $\text{Ca}^{2+}$   | 0.897**          | 1                |              |               |                 |                    |                 |         |    |
|      | $\text{K}^+$       | 0.226            | 0.457*           | 1            |               |                 |                    |                 |         |    |
|      | $\text{Cl}^-$      | 0.532*           | 0.663**          | 0.598**      | 1             |                 |                    |                 |         |    |
|      | $\text{NO}_3^-$    | 0.468*           | 0.677**          | 0.712**      | 0.796**       | 1               |                    |                 |         |    |
|      | $\text{SO}_4^{2-}$ | 0.097            | 0.358            | 0.874**      | 0.552*        | 0.770**         | 1                  |                 |         |    |
|      | $\text{NH}_4^+$    | 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 <sup>2+</sup> | Ca <sup>2+</sup> | K <sup>+</sup> | Cl <sup>-</sup> | NO <sub>3</sub> <sup>-</sup> | SO <sub>4</sub> <sup>2-</sup> | NH <sub>4</sub> <sup>+</sup> | OC      | EC |
| Mg <sup>2+</sup>              | 1                |                  |                |                 |                              |                               |                              |         |    |
| Ca <sup>2+</sup>              | 0.721**          | 1                |                |                 |                              |                               |                              |         |    |
| K <sup>+</sup>                | 0.191            | 0.407            | 1              |                 |                              |                               |                              |         |    |
| Cl <sup>-</sup>               | -0.061           | 0.316            | 0.519*         | 1               |                              |                               |                              |         |    |
| NO <sub>3</sub> <sup>-</sup>  | -0.241           | 0.161            | 0.579**        | 0.642**         | 1                            |                               |                              |         |    |
| SO <sub>4</sub> <sup>2-</sup> | -0.133           | 0.109            | 0.458*         | 0.482*          | 0.744**                      | 1                             |                              |         |    |
| NH <sub>4</sub> <sup>+</sup>  | -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  |

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

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826 **Table 5.** The correlations between [Zn] vs. [Cu] and [As] vs. [Se] in PM<sub>2.5</sub> at the four sampling  
 827 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**    |

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

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