A point-by-point response to the reviews

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

Response to Co-Editor

Comment 1: The authors have addressed the scientific comments by the two referees in sufficient detail. After reading the revised paper by myself, I have several (mostly technical) issues that still should be corrected before accepting this paper for publication.

Answer: Thank you very much for your appreciation. The followings are our responses to your comments.

Comment 2: First, in section 3.4 and elsewhere, the authors should not confuse between the strength (R values) and significance (p values) of the correlations when discussing the results. Now, throughout section 3.4, the authors refer to significance of the correlation even though in most cases it is actually the strength of the correlation that is meant (e.g. in figure 10 the correlation is moderate to strong for 6 cases and non-existent for the 2 other cases). Please correct.

Answer: Thank you for your valuable guidance. The strength and significance of the correlations have been distinguished in our revised manuscript. When discussing the R values, "the significant correlations" has been revised as "the strong correlations"; when discussing the p values, the p values has been inserted in the manuscript.

Comment 3: Second, the comparison of percentages on lines 541-545 is not quite correct. E.g. if the proportion in A is 12% and in B it is 10%, then this proportion is not 2% higher in A compared with B. Please give only absolute percentages of these proportions, and when comparing different sites, simple state qualitatively to which direction they are between different sites (e.g. slightly larger than…).

Answer: Thank you for your valuable comment. The sentence has been rephrased as "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 **much** greater than those **(37.9 % for OC and 7.4 % for EC)** 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 **slightly** less than those (15.1 % for NO_3^- and 14.0 % for SO_4^{2-}) at BJ, respectively." in our revised manuscript.

Comment 4: Third, there are a number of sentences that are unclear and should be modified, either grammatically or otherwise. I list their locations below:

320-323

Answer: "the promotion new stoves" has been revised as "the promoted new stoves".

480-481 (what is meant by fluctuating trends?)

Answer: "exhibited similar fluctuation trends" has been revised as "exhibited similar trend".

487 (are you referring to pollutant concentrations here, please specify)

Answer: "spatial and temporal difference of pollutants" has been revised as "spatial and temporal

difference in concentrations of pollutants".

505-507

Answer: The sentence has been rephrased as "Compared with the cities, the distinct source for atmospheric pollutants at DBT in winter is the residential coal combustion **because residential coal combustion** is prevailingly used for heating and cooking in rural areas of the Northern China."

528-530 (high density of countryside?)

Answer: "high density of countryside" has been revised as "countryside with high farmer density".

569-571

Answer: The sentence has been rephrased as "Because **the average concentrations of the species in $PM_{2.5}$ were mainly controlled by the highest concentration values and the relatively high concentration level of the species in $PM_{2.5}$ at BJ usually occurred during the serious pollution episodes**, the proportions of the species in $PM_{2.5}$ were dominated by the serious pollution events."

588-590

Answer: The sentence has been rephrased as "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 **and, however, the OC/EC ratios observed** 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)."

685-687

Answer: The sentence has been rephrased as "**If the primary $PM_{2.5}$ was only 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."

Comment 5: Finally, there are a number of minor technical and grammatical issues that should be corrected:

Throughout the paper: difference in, not of

Line 271: …sites were almost the same (4.8) when ….

277-278: …rural areas, whereas…transportation, were…

290-291: … matter with an aerodynamic diameter…

303: …levels can still be larger than 1000…

309: … combustion, which … region, was…

324: There are…

338-340: please delete the last 4 "the" from the list (only the first one should be there). Also delete "method" from the end.

364: delete "p.m." 15:00 already reveals that it is in the afternoon

367: 10 mL of ultrapure

369: … before the analysis, and the …

374: … 10%, and the ….

377: in the same way

383: A chemical mass closure…

438-440: Meteorological data, including…temperature and barometric pressure, as well as air quality index (AQI) based on PM … and WD, were obtained….

450: …for each sampling day.

465: delete “obviously”. The values are, or are not, positive.
481: differences
483: especially the wind speed
488-489: …considered similar because…
508-509: …due to the lack of any control measures, as strong…
513-514: please move the citation to the end of this sentence
515-516: … process can be as high as… (Is this what you mean here?)
575: should this be “relations” rather than “correlations”?
584-585: …a dominant…periods.
594: … very reactive, favoring secondary organic aerosol (SOA) formation (Zhang…)
600: …would be smaller during…
630: have been reported to be…
632: which is at least…

Answer: Thank you very much for your careful reviews. These mistakes have been corrected in our revised manuscript:
Throughout the paper: “difference of” has been revised as “difference in”
Line 271: “…sites became the almost same value of 4.8…” has been revised as “…sites were almost the same (4.8) when …”
277-278: The sentence has been rephrased as “…residential coal combustion was **the** dominant source for the key species in the rural area **and, however,** the complex sources including local emissions and regional transportation were **responsible** for **the** atmospheric species in the cities”
290-291: “…fine particulate matters with dynamic diameter…” has been revised as “…matter with an aerodynamic diameter…”
303: “…levels still achieved to be above…” has been revised as “…levels can still be larger than…”
309: “…combustion which … region was…” has been revised as “…combustion, which … region, was…”
324: “There were…” has been revised as “There are…”
338-340: The sentence has been rephrased as “…based on the $PM_{2.5}$ levels, $PM_{2.5}$ composition characteristics, correlations among key species in $PM_{2.5}$, back trajectories and chemical mass closure.”
364: “p.m.” has been deleted in our revised manuscript
367: “…10 mL ultrapure…” has been revised as “…10 mL of ultrapure…”
369: “… before analysis and the …” has been revised as “… before the analysis, and the …”
374: “… 10% and the ….” has been revised as “… 10%, and the ….”
377: “as the same way” has been revised as “in the same way”
383: “Chemical mass closure…” has been revised as “A chemical mass closure…”
438-440: Both the meteorological data, including …temperature, barometric pressure and air quality index (AQI) of PM … and WD were obtained….” has been revised as “Meteorological data, including…temperature and barometric pressure, as well as air quality index (AQI) based on PM … and WD, were obtained….”
450: “respectively” has been deleted in our revised manuscript
465: “obviously” has been deleted in our revised manuscript
481: “…there was obvious difference…” has been revised as “…there were obvious differences…”

483: “especially wind speed…” has been revised as “especially the wind speed…”

488-489: “…considered as the same because…” has been revised as “…considered similar because…”

508-509: “…due to lack of any control measures, strong…” has been revised as “…due to the lack of any control measures, as strong…”

513-514: the citation has been moved to the end of this sentence in our revised manuscript

515-516: “…process could achieve to be” has been revised as “… process can be as high as…”

575: “correlations” has been corrected as “relations”

584-585: “…made dominant contribution…” has been revised as “…made a dominant contribution…”

594: “…very reactive to make contribution to secondary organic aerosols (SOA) (Zhang…)” has been revised as “… very reactive, favoring secondary organic aerosol (SOA) formation (Zhang…)”

600: “…would become less during…” has been revised as “…would be smaller during…”

630: “were reported to be…” has been revised as “have been reported to be…”

632: “…which were at least…” has been revised as “…which is at least…”

Thank you very much for all you’ve done for us.

A list of all relevant changes made in the manuscript

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

1. The strength and significance of the correlations have been distinguished and corrected in our revised manuscript.
2. The discussion about the comparison of percentages has been improved in our revised manuscript.
3. A number of sentences that were unclear have been modified and rephrased in our revised manuscript.
4. Many logical and grammatical mistakes have been corrected 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~~ were almost the same value ~~of~~ (4.8) when the concentrations of $PM_{2.5}$ were greater than 150 μg 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 ($p < 0.05$) from the countryside to the cities further confirmed that residential coal combustion was the ~~preferentially~~ dominant source for the key species in the rural area and, however, ~~whereas~~ the complex sources including local emissions and regional transportation were ~~dominant~~ responsible for the atmospheric species in the cities. The ~~significant~~ strong correlations among OC, EC, Cl^-, NO_3^-, and NH_4^+ were found at the four sampling sites but only ~~significant~~ strong 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 matter~~s~~ with ~~dynamic~~ an aerodynamic 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~~ can still be larger than 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 42 Tg/year) 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~~ implementation strength of the control measures is still very limited. Additionally, the ~~promotion~~ promoted 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~~ are 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})

306 in the northern China. Duan et al. (2012) inferred that the lower OC/EC ratios at the rural site than
307 at the urban site were ascribed to coal combustion prevailed in the rural area. Our previous study
308 revealed that residential coal combustion made evident contribution to atmospheric water-soluble
309 ions (WSIs) in Beijing (P. Liu et al., 2016). Based on Weather Research and Forecasting model
310 coupled with Chemistry, J. Liu et al. (2016) recently estimated that the residential sources (solid
311 fuel) contributed 32 % and 53 % of the primary $PM_{2.5}$ emissions in the BTH region during the whole
312 year and during the winter of 2010, respectively.
313 In this study, daily samples of $PM_{2.5}$ were simultaneously collected at the four sampling sites
314 (Beijing City, Baoding City, Wangdu County and Dongbaituo Countryside) during the winters and
315 springs of 2014-2015, and the direct evidence for the influence of residential coal combustion on
316 regional $PM_{2.5}$ in the region was found based on the $PM_{2.5}$ levels, ~~the~~ $PM_{2.5}$ composition
317 characteristics, ~~the~~ correlations among ~~the~~ key species in $PM_{2.5}$, ~~the~~ back trajectories and ~~the~~
318 chemical mass closure ~~method~~.

319 **2 Materials and methods**

320 **2.1 Sampling sites**

321 The two sampling sites in Beijing City and Dongbaituo Countryside, which have been described in
322 detail by our previous study (P. Liu et al., 2016), were selected on a rooftop (approximately 25 m
323 and 5 m above ground, respectively) of the Research Center for Eco-Environmental Sciences,
324 Chinese Academy of Sciences (RCEES, CAS) and a field station in the agricultural field of
325 Dongbaituo village, Baoding, Hebei Province, respectively. Another two sampling sites in Baoding
326 City and Wangdu County were both chosen on the rooftop of local environmental monitor station
327 (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 locations of the four sampling sites 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 was carried out from January 21 to February 10, 2015 and $PM_{2.5}$ samples were collected in the same way on the quartz fiber filters (90 mm, Munktell). 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 of ultrapure water for half an hour. The solutions were filtered through a micro-porous membrane (pore size, 0.45 μm; diameter, 13 mm) before the 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 ~~as~~ in 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

A 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 sea salt (Brewer, 1975; van Eyk et al., 2011), 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). 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:

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

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

$$\frac{[Cl_{cc}^{-}]/35.5}{[Na_{cc}^{+}]/23} = 1.4 \quad (3)$$

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

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 (Blasing 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:

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

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:

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

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

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):

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

where $([Element]/[Al])_{aerosol}$ is the ratio of the element to Al in aerosols and $([Element]/[Al])_{crust}$ 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:

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

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 m~~ Meteorological data, including wind speed, wind direction, relative humidity (RH), temperature, barometric pressure ~~and~~, as well as air quality index (AQI) ~~of~~ based on $PM_{2.5}$, 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 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 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 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~~ in 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~~ trend~~s~~ (Fig. 6), but there ~~was~~ were obvious difference~~s~~ ($p < 0.01$) 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 the wind speed and planetary boundary layer (PBL), play pivotal roles in 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 in concentrations of pollutants. As for the sampling sites of BD, WD and DBT, the meteorological conditions could be considered similar ~~as the same~~ because of the short distances (< 36 km) among them, and hence the spatial difference in the concentrations 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~~ in 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 in the concentrations 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~~ in 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 in the concentrations of the pollutants. 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~~ because residential coal combustion 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 the lack of any control

481 measures, as strong smoke could be seen in the chimney of the residential coal stoves. The emission
482 factors of OC and EC from residential coal combustion were reported to be 0.47-7.82 g kg^{-1} coal
483 and 0.028-2.75 g kg^{-1} coal, respectively (Chen et al., 2005; Zhang et al., 2008). The emission factors
484 of various pollutants from a typical residential coal stove fueled with raw bituminous coal were also
485 investigated in our group ~~(Du et al., 2016; Liu et al., 2017)~~ according to farmers' customary uses of
486 coal stoves under the alternation cycles of flaming and smoldering (Du et al., 2016; Liu et al., 2017).
487 The emission factors of OC and EC under the entire combustion process can be as high as ~~could~~
488 ~~achieve to be~~ 10.99 ±0.95 g kg^{-1} coal and 0.84 ±0.06 g kg^{-1} coal, respectively (Table 3). Considering
489 the high density of farmers in the rural area, the largest levels of atmospheric OC and EC at DBT
490 could be rationally ascribed to residential coal combustion. However, the proportion of the WSIs
491 from residential coal combustion (Fig. 7a) were extremely low with respect to that of the atmosphere.
492 Therefore, the largest levels of the key WSIs in $PM_{2.5}$ at DBT were suspected to the secondary
493 formation via the heterogeneous or multiphase reactions which might be accelerated by the OC and
494 EC particles (Han et al., 2013; Zhao et al., 2016) emitted from residential coal combustion.
495 Although the three sampling sites of DBT, WD and BD are closely adjacent, the lowest
496 concentrations of the key species in $PM_{2.5}$ were observed at WD, which was probably ascribed to
497 the replacement of coal with natural gas for the central heating in the county of WD (a main pipe of
498 natural gas is just across the county), e.g., the average concentration of NO_2 was higher at WD than
499 at BD, whereas the average concentration of SO_2 was on the contrary (Table 2).
500 The city of BD and the county of WD are fully surrounded by ~~high density of~~ countryside with high
501 farmer density, whereas the city of BJ is only neighbored with ~~high density of~~ the countryside in the
502 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~~ much greater than those (37.9 % for OC and 7.4 % for EC) 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 %~~ slightly less than those (15.1 % for NO_3^- and 14.0 % for SO_4^{2-}) at BJ, respectively. The obvious differences ~~of~~ in 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 average concentrations of the species in $PM_{2.5}$ were mainly controlled by the highest concentration values and the relatively high concentration level of the species in $PM_{2.5}$ at BJ usually occurred 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

547 the four sampling sites might be partly ascribed to the conversions of NO_2 and SO_2 to NO_3^- and
548 SO_4^{2-} during the air parcel transportation from the south-southwest directions. The contribution of
549 the transportation to atmospheric OC and EC at BJ could be verified by the ~~cor~~relations between
550 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
551 were almost independent of the $PM_{2.5}$ levels, whereas the OC/EC ratios at BJ and BD remarkably
552 decreased with increasing the $PM_{2.5}$ levels and reached the almost same value (about 4.8 ± 0.5) as
553 those at WD and DBT when the concentrations of $PM_{2.5}$ were above 150 μg m^{-3} (the serious
554 pollution events). Because there were relatively sparse emissions from vehicles and industries at
555 WD and DBT, the almost constant of OC/EC ratios under the different levels of $PM_{2.5}$ at WD and
556 DBT further revealed that atmospheric OC and EC were dominated by the local residential coal
557 combustion. The almost same OC/EC ratios at the four sampling sites with the concentrations of
558 $PM_{2.5}$ greater than 150 μg m^{-3} indicated that the residential coal combustion also made a dominant
559 contribution to atmospheric OC and EC in the two cities during the severe pollution period. Our
560 previous study (C. Liu et al., 2016) also found that the contribution from residential coal combustion
561 to atmospheric VOCs increased from 23 % to 33 % with increasing pollution levels in Beijing.
562 It should be mentioned that the OC/EC ratios observed at DBT and WD were about a factor of 2.7
563 less than that (13.1) of the emission from the residential coal combustion and, ~~whereas~~ however, the
564 OC/EC ratios observed at BJ and BD were too high to be explained by direct emissions from diesel
565 (0.4-0.8) and gasoline (3.1) vehicles (Shah et al., 2004; Geller et al., 2006). The OC emitted from
566 the residential coal combustion might be easily degraded or volatilized in the atmosphere, resulting
567 in the relatively low OC/EC ratios observed at DBT and WD. In China, aromatic compounds as
568 typical pollutants from vehicle emissions are very reactive, ~~to make contribution to~~ favoring

secondary organic aerosols (SOA) formation (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~~ be smaller 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 ($p < 0.05$) 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~~ strong 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~~ strong correlations among OC, EC, NO_3^-, NH_4^+ and Cl^- were found at the four sampling sites, whereas the ~~significant~~ strong 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~~ strong correlations among OC, EC, NO_3^-, NH_4^+ and Cl^- but the ~~insignificant~~ non-existent 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~~ have been 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~~ is 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~~ strong 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~~ moderately strong correlation between [Pb] and [Cu+Zn] but non-existent 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~~ moderately strong correlations between [Pb] and [Cu+Zn] as well as [Pb] and [As+Se] were found at the two sampling sites. Although there was non-existent 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

635 which has been described in detail in section 2.3. The average proportions of the species from
636 different sources in $PM_{2.5}$ during the sampling period at the four sampling sites are comparatively
637 shown in Fig. 11. It is evident that secondary aerosols (SIA + SOC) accounted for the largest
638 proportion (about 32-41 %) in $PM_{2.5}$, followed by POC (about 24-28 %), EC (about 6-8 %), mineral
639 dust (about 2-8 %) and Cl^-_{cc} (about 2-5 %) at the four sampling sites. The proportion of mineral dust
640 was the highest at BJ and the lowest at DBT among the four sampling sites, whereas the proportion
641 of Cl^-_{cc} was on the contrary. Because the concentrations of the mineral dust compounds were much
642 higher under stagnant weather condition than under clean days at BJ, the remarkably high proportion
643 of mineral dust at BJ was mainly ascribed to the emissions from road dust and construction (Liang
644 et al., 2016) during the sampling period. The obviously high proportion of Cl^-_{cc} at DBT was ascribed
645 to the emission from residential coal combustion (Shen et al., 2016). In addition, the proportions of
646 TEO, K^+_{bb} and Cl^-_{ss} were less than about 2 %, which were insignificant to the sources of $PM_{2.5}$ at
647 the four sampling sites during the sampling period.
648 Atmospheric Primary Organic Matters (POM) and Cl^-_{cc} at the four sampling sites could be estimated
649 based on POM≈POC × 1.6 (Cheung et al., 2005; Hsu et al., 2010b; Han et al., 2015) and the
650 formulas (1)-(4), respectively. The sum of POM, EC and Cl^-_{cc} at DBT was assumed to be solely
651 from residential coal combustion, accounting for about 58% in $PM_{2.5}$ (Fig. 12). Assuming that the
652 ratio of Cl^-_{cc} to the sum of POM, EC and Cl^-_{cc} was constant for coal combustion at the four sampling
653 sites, the primary contribution of coal combustion to atmospheric $PM_{2.5}$ at BJ, BD and WD could
654 be estimated to be 32 %, 49 % and 43 % (Fig. 12), respectively. The annual residential coal
655 consumption mainly focused on the four months in winter, accounting for about 11 % of the total
656 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 only 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** 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

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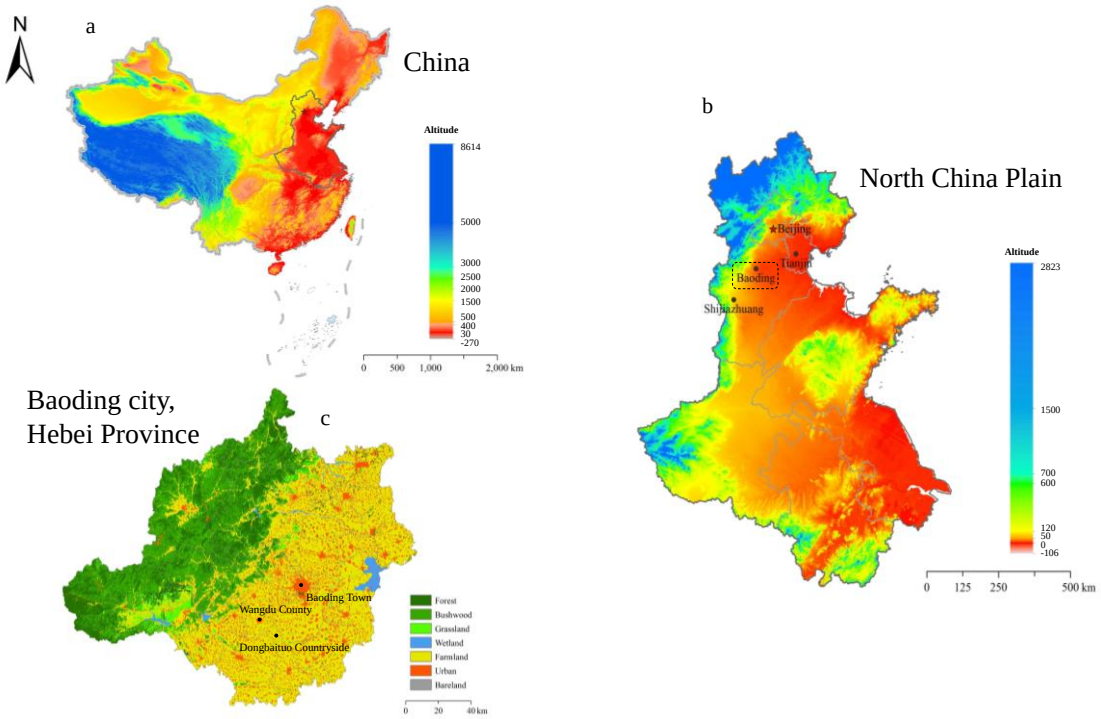

Figure 1. China (a), the North China Plain (b) and Baoding city in Hebei Province (c). The locations of sampling sites (BJ, BD, WD and DBT) as well as Tianjin municipality and Shijiazhuang as provincial capital of Hebei are marked.

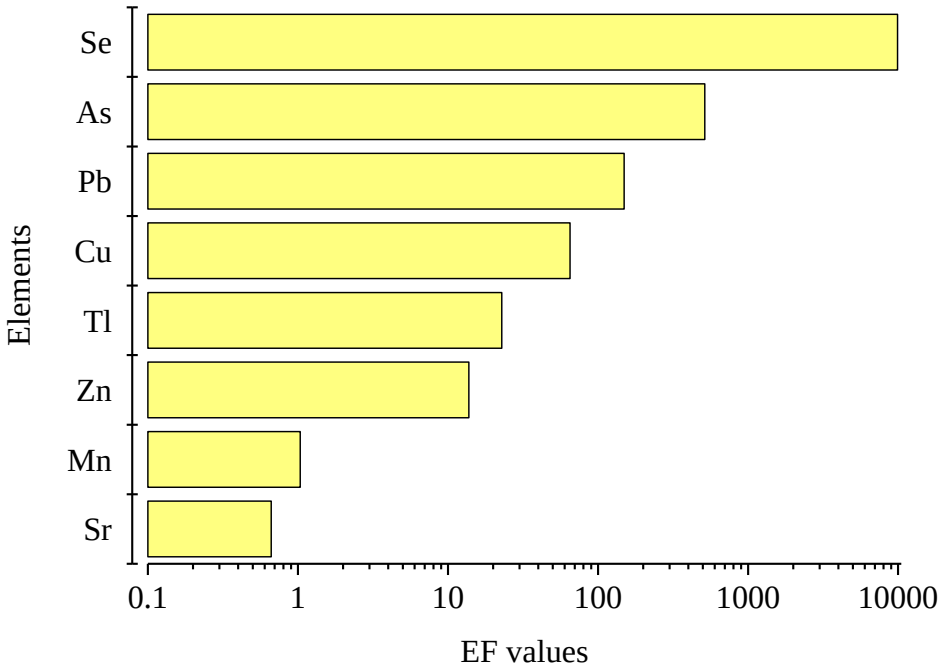

Figure 2. Enrichment factor values for trace elements in $PM_{2.5}$.

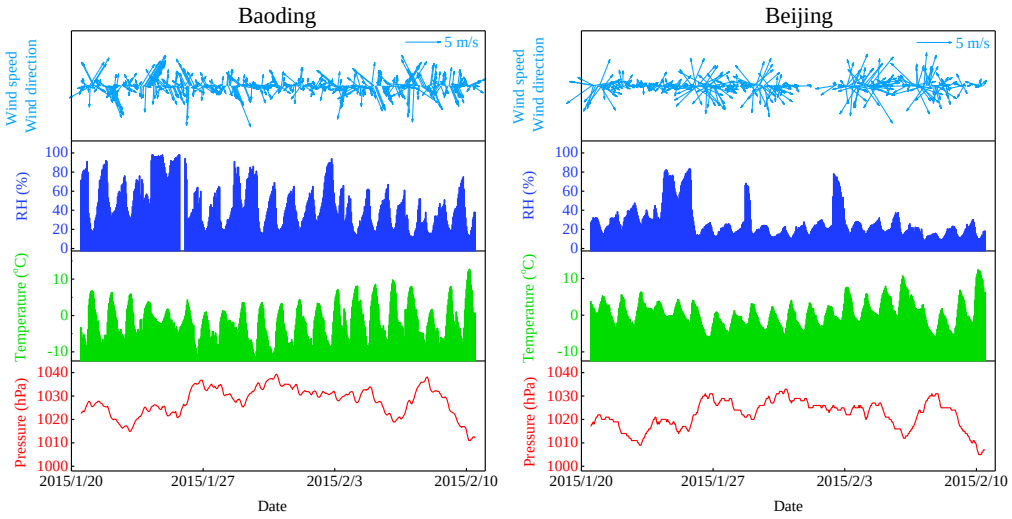

Figure 3. The wind speed, wind direction, RH, temperature and barometric pressure at BD and BJ during the sampling period in the winter of 2015.

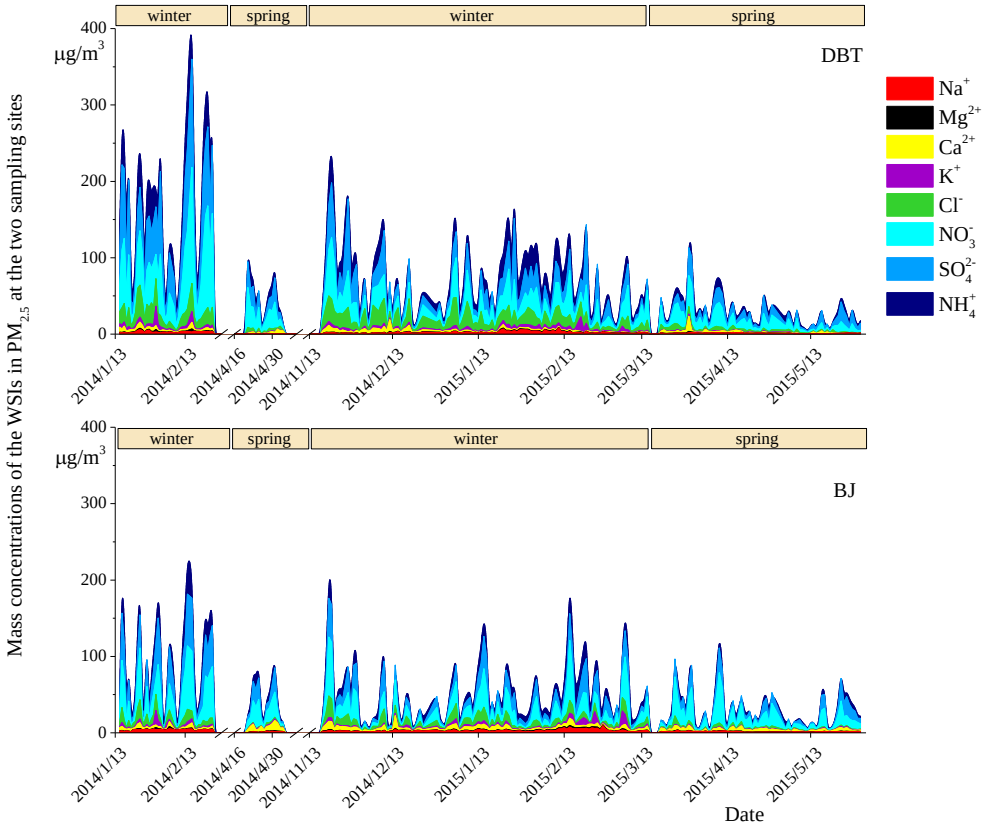

Figure 4. The mass concentrations of the WSIs in $PM_{2.5}$ at DBT and BJ during the sampling period in the winters and springs of 2014-2015.

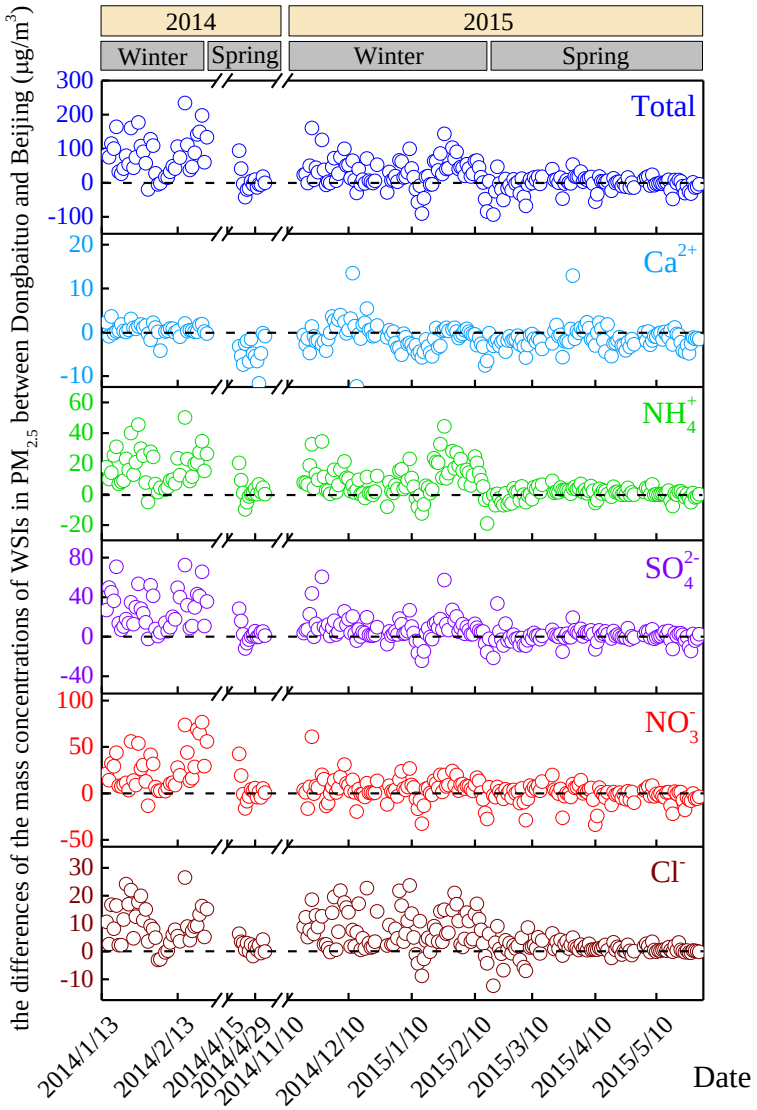

Figure 5. The D-values of the mass concentrations of WSIs in $PM_{2.5}$ between DBT and BJ during the sampling period in the winters and springs of 2014-2015.

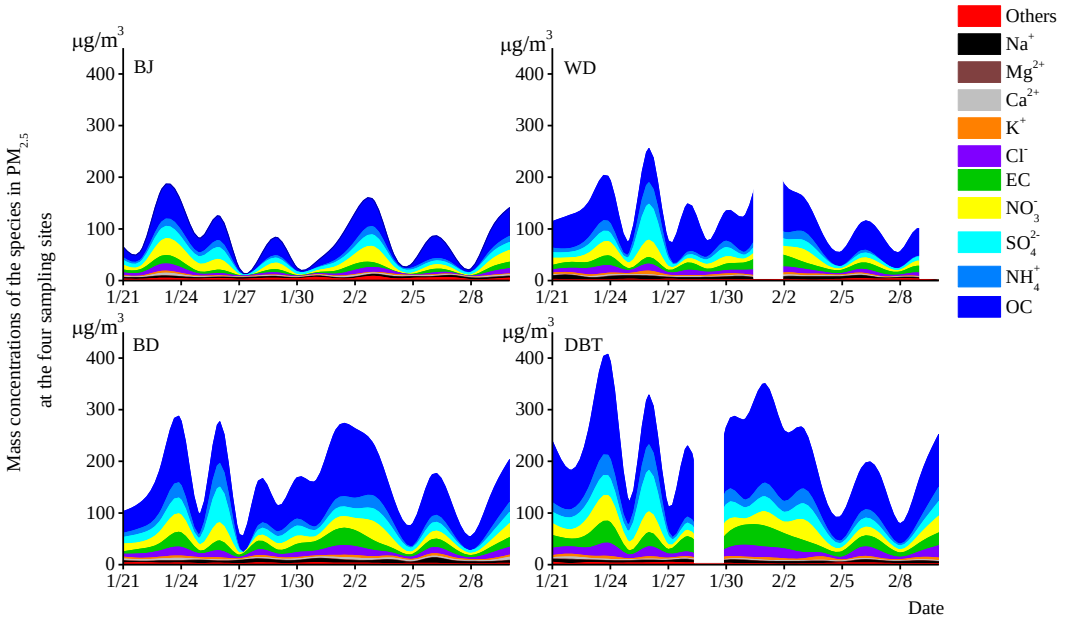

Figure 6. Daily variation of the species in $PM_{2.5}$ at the four sampling sites during the sampling period in the winter of 2015.

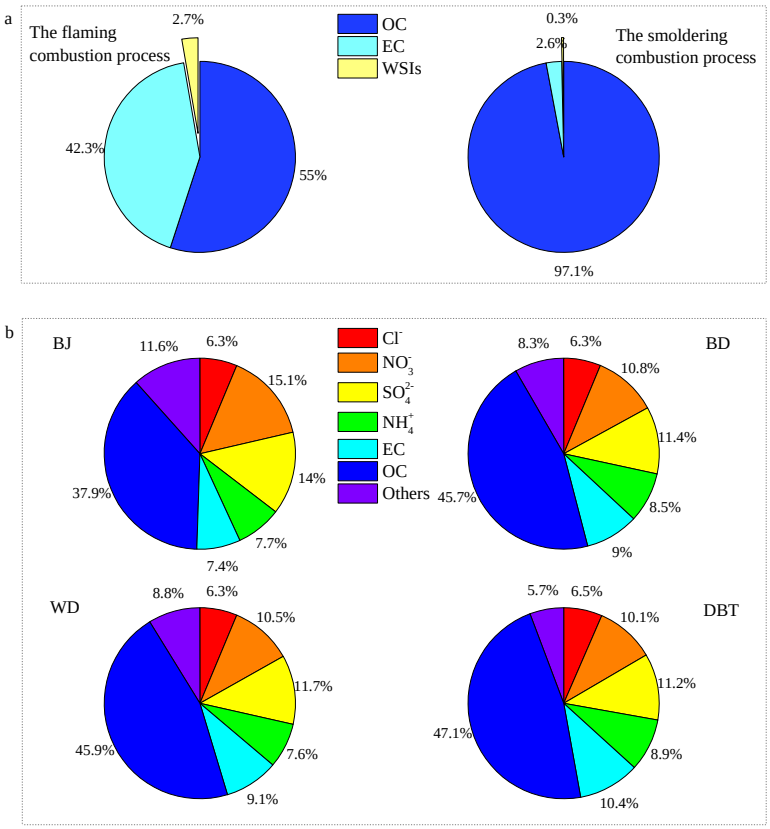

Figure 7. The mass proportions of OC, EC and WSIs from residential coal combustion under the flaming and smoldering combustion processes (a), and the average mass proportions of the typical

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

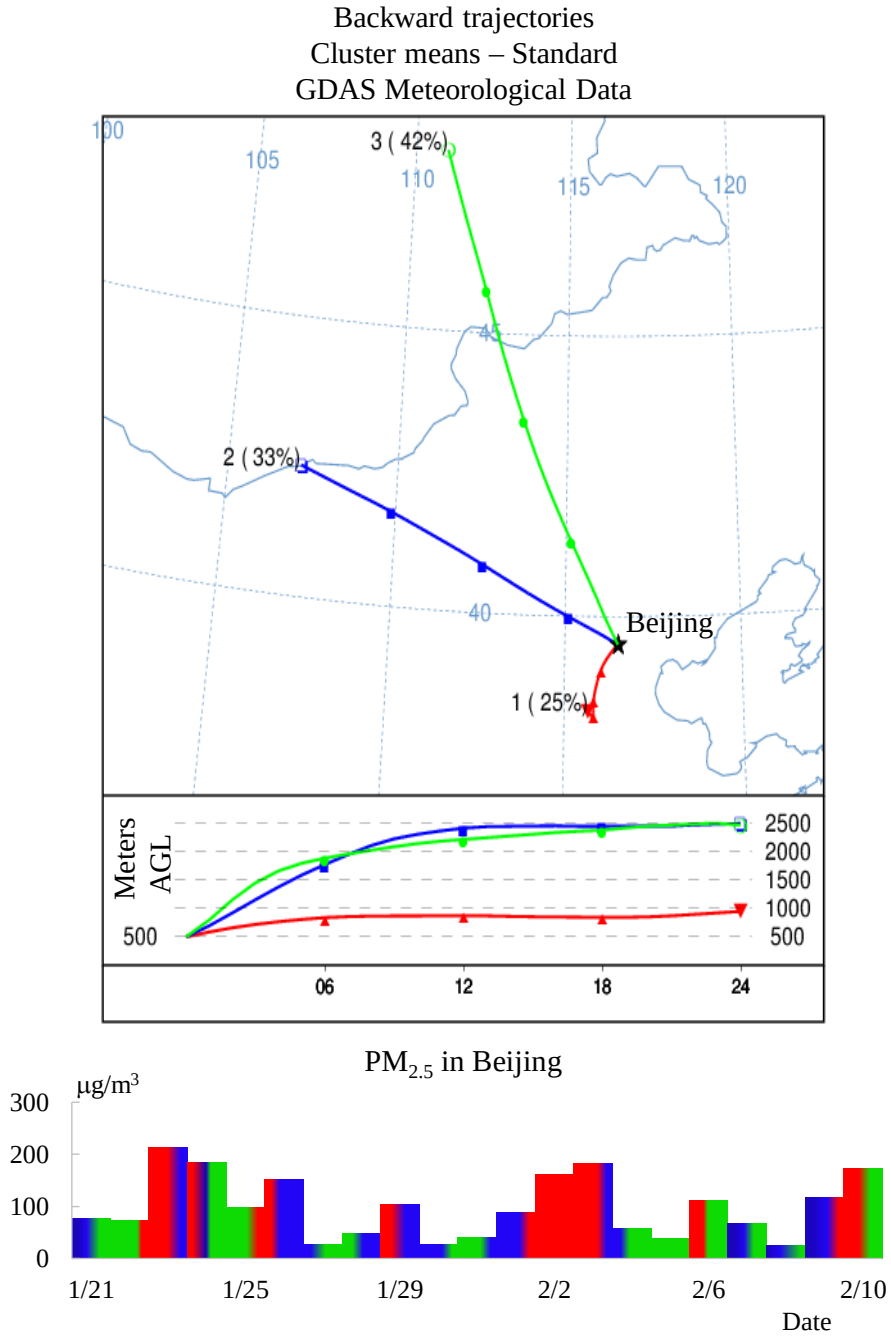

Figure 8. The back trajectory cluster analysis and the corresponding $PM_{2.5}$ concentrations in Beijing during the sampling period in the winter of 2015.

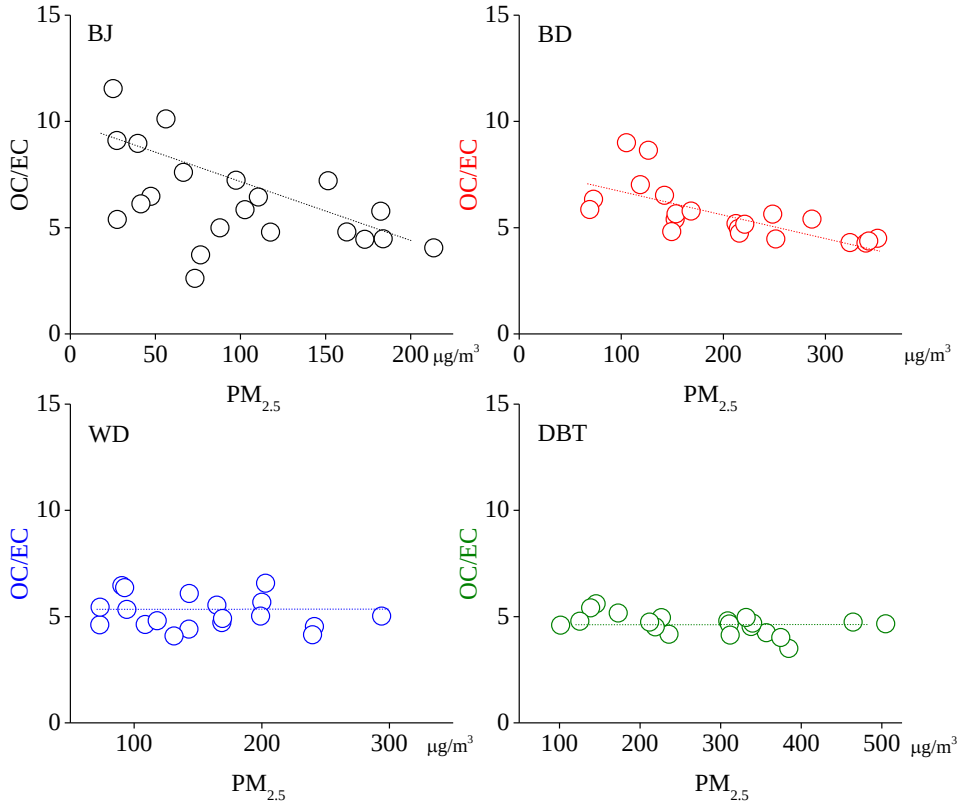

Figure 9. The correlations between the OC/EC ratios and the $PM_{2.5}$ concentrations at the four sampling sites during the sampling period in the winter of 2015.

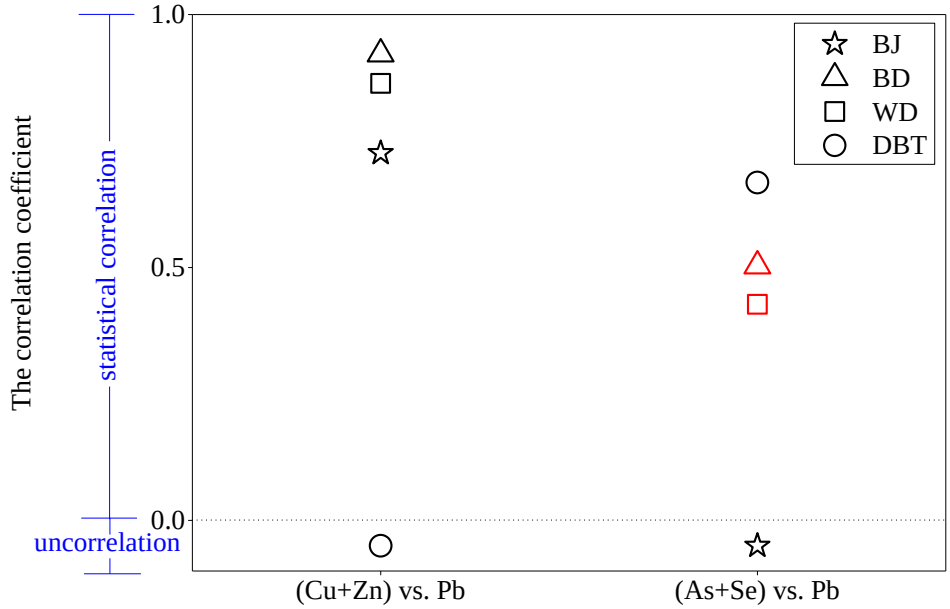

Figure 10. The statistical correlations for [Cu+Zn] vs. [Pb] and [As+Se] vs. [Pb] in $PM_{2.5}$ at the four sampling sites during the sampling period in the winter of 2015. The uncorrelated results are

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

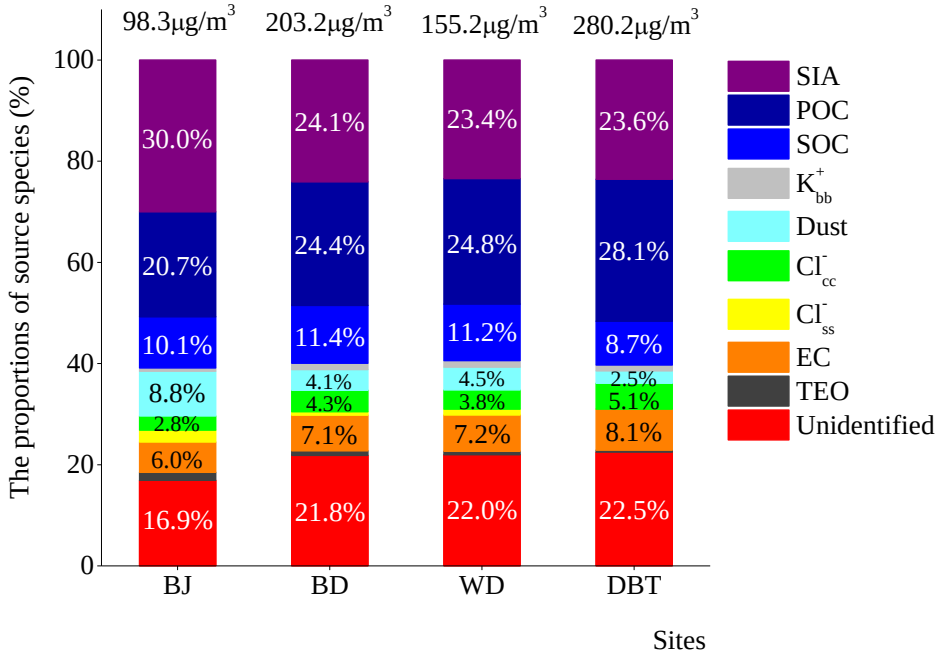

Figure 11. The proportions of source species under the constructed chemical mass closures for $PM_{2.5}$ at the four sampling sites during the sampling period in the winter of 2015. Average mass concentrations of $PM_{2.5}$ at each sampling site, including all of source species and unidentified fractions,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

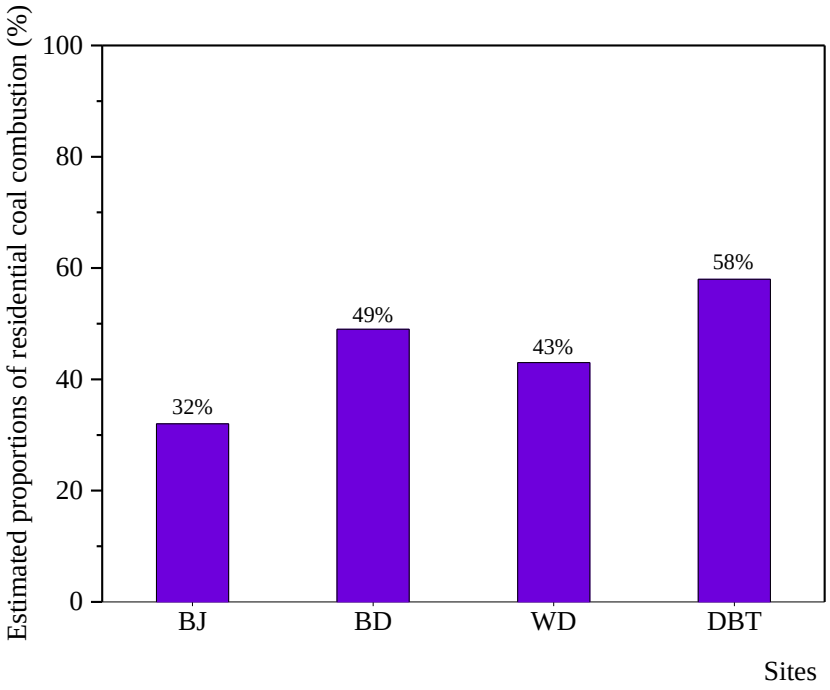

Figure 12. The estimated contributions of coal combustion to the $PM_{2.5}$ at the four sampling sites during the sampling period in the winter of 2015.

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	-

1072 **Table 3.** The emission factors (Mean ± SD) (g kg^{-1} coal) of OC and EC from residential coal
1073 combustion during the flaming combustion process, the smoldering combustion process and the
1074 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

1075

1076 **Table 4.** The correlations of several typical species in $PM_{2.5}$ at the four sampling sites during the
1077 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.