Characterization of $PM_{2.5}/PM_{2.5-10}$ and source tracking in the juncture belt between urban and rural areas of Beijing

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Coarse ($PM_{2.5-10}$) and fine ($PM_{2.5}$) atmospheric particulate samples were collected in summer and winter during 2005–2007 in the juncture belt between urban and rural areas of Beijing. Elements, ions, organic/elemental carbon (OC/EC) and polynuclear aromatic hydrocarbons (PAHs) were determined to obtain some latest information about the particulate pollution in the juncture belt of Beijing. Particulate matter levels at this site were high as compared with the levels at other sampling sites in Beijing. Pollution elements, secondary ions and PAHs were enriched in fine particles rather than in coarse particles. An obvious seasonal variation of the chemical composition of PM was observed. Source apportionment results showed that secondary components were the largest mass contributor of $PM_{2.5}$, accounting for 28%; whereas soil-related sources were the largest contributor of $PM_{2.5-10}$, explaining about 49% of the total mass. The abnormal levels of soil heavy metals at the electronic waste disassembly site in the upwind villages suggested the potential impact of such activities to the environment.

$PM_{2.5-10}$, $PM_{2.5}$, source apportionment, electronic waste pollution

There is growing concern about the environmental effects of airborne particulate matter. Inhalable particulate matter has long been known to have adverse health effects such as respiratory diseases and increased mortality^[1,2]. Asian dust particles through long-range transport from China mainland to the Pacific and the western coast of America not only can affect the global radiation energy balance^[3,4], but also can influence the primary productivity of the Ocean and the global carbon budget as well^[5,6].

Many papers have been published on the characterization of particulate matter in Beijing before the 2008 Olympic Games to be held in this city. There is no systematic record of $PM_{2.5}$ levels in Beijing, as air quality standard for $PM_{2.5}$ has not been established in China. Fragmented data available for the $PM_{2.5}$ concentrations in Beijing show high levels of fine particles in ambient air potential for adverse effects. An early $PM_{2.5}$ study in 1999–2000^[7] showed the average values of $114 \mu\text{g}/\text{m}^3$

at the Chegongzhuang site and $127 \mu\text{g}/\text{m}^3$ at the Tsinghua site. A recent paper in 2005^[8] reported that the annual average concentration of $PM_{2.5}$ measured in Beijing was $101 \mu\text{g}/\text{m}^3$. In comparison, the measured average concentration of $PM_{2.5}$ was only $21 \mu\text{g}/\text{m}^3$ in Houston^[9], $14.4 \mu\text{g}/\text{m}^3$ in Pittsburgh^[10], and $21.0 \mu\text{g}/\text{m}^3$ in Baltimore^[11] in the US, and ranged from 3.7 to $44.9 \mu\text{g}/\text{m}^3$ in 21 European study centers^[12].

Meanwhile, the focus of PM studies in Beijing has been shifted from inorganic compositions to organic markers, such as levoglucosan, PAHs, fatty acids, dicarboxylic acids, alkanes, hopanes, carbonaceous matter, and others^[13–18]. Source apportionment with the aid of

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Varimax FA, CMB and PMF software was performed too for the identification of PM sources^[19–22]. However, receptor modeling based upon limited numbers of samples (usually around 100 samples) and short duration of monitoring (usually 1 year) could give only some generic source categories in Beijing, such as re-entrained soil dust, vehicular emissions, coal combustion, biomass combustion and industrial emissions in general. Although there have been studies on the spatial variation of PM compositions in various functional districts of Beijing like commercial, industrial, residential, rural, traffic junction^[20,21], relatively rare special attention has been paid to the juncture belt between the urban and rural areas of Beijing, where millions of non-permanent population concentrate and coal is used for space heating and cooking. So far, no further source tracking on such emerging area sources or unknown industrial sources in Beijing has been reported.

Our 3-phase project (2001–2010) supported by SIDA focused on this gap—long-term simultaneous sampling and analyses of PM_{2.5} and PM_{2.5–10} at urban, suburban and background sites, as well as source apportionment and subsequent tracking of overlooked sources^[23]. This article describes some of our findings during the second phase of the project (2005–2007) on PM levels, composition and possible source contributions with 210 samples collected at a suburban sampling site in the juncture belt of Beijing.

1 Experimental

1.1 Description of the sampling site

PM_{2.5} and PM_{2.5–10} were collected on the rooftop of a research building (18 m high) in the Research Center for Eco-environmental Sciences (RCEES), which is located in on the campus of the Beijing Forestry University, the northwest suburb of Beijing (Figure 1). On the east and south sides of RCEES, newly finished modern teaching and outreach buildings of several universities as well as new residential quarters have emerged, and nature gas is the main energy used for cooking and heating. Nevertheless, on the north and west sides of RCEES (i.e., the upwind directions) there are shabby cottages of villages bearing the names of Front Bajia and Back Bajia with a total area of about 1.5 km² and a population about 20 thousand. About ten years ago, the farmland in the suburbs of Beijing was converted gradually into housing estates. The farmers, after deprived of their land, were

Figure 1 Layout of PM, dust and soil sampling locations. A, PM and rooftop dust sampling site on a RCEES building; B, soil in the yard of an electronics disassembling shop; C, soil in the campus of Beijing Forestry University; D, soil in front of a waste recycling point; E, soil from a waste disposal station; F, soil in front of a small restaurant; G, soil in front of a curbside waste collection site; H, soil in front of a curbside metal workshop.

no longer involved in agricultural production, but rented out their tenement to temporary laborers engaged in collection and disassembly of electronic wastes, metal-working and other business, and people engaged in recycling wastes—including the electronic wastes take a proportion of 60% of the total Bajia population. Due to the poverty, local high S-containing coal and wood are their main energy used for cooking and heating, which could result in high PM pollution. Usually, Bajia is regarded as one of the four juncture belts between the urban and rural areas of Beijing. RCEES, due to its very close distance to Bajia area, could be looked as the right site for the PM study of this special area.

1.2 Sampling

Two low-volume samplers (Sierra 244, US) were employed for PM_{2.5} and PM_{2.5–10} collection at a constant flow rate of 16.7 L/min, and were calibrated before sampling. Samples were collected for 24 h per day in summer (Jul. 1–30) and winter (Dec. 15–Jan. 15). Fiber filters (Whatman 41, UK) and quartz filters (QR100, Advantec, Japan) were used for the analyses of elements/ions and organic compounds, respectively. Totally, 210 samples were collected in this campaign. After sampling, these filters were put into the polyethylene plastic bag immediately and stored in refrigerator, then weighed under constant temperature (20 ± 5 °C) and humidity (40% ± 2%), using an analytical balance (Sartorius 2004 MP, Germany) with a reading precision of 10 µg. All these steps were strictly quality-controlled to avoid any possible sample contamination.

In addition, soil samples of the 0–5 cm layers were collected at seven points surrounding the PM sampling site (Figure 1). Each of the soil samples was mixed well, sieved through 100-mesh sieves to remove any bulky matter, and subjected to elemental analysis with the aid of ICP/OES after dissolution. Dust sample was also collected on the rooftop of the same research building in RCEES, sieved and subjected to analysis in the same way.

1.3 Chemical species characterization

Each Whatman filter was cut into two equal pieces for inorganic analyses: one half for the determination of 21 elements (K, Ca, Ti, V, Cr, Mn, Fe, Ni, Co, Cd, Cu, Zn, As, Se, Mg, Sr, Pb, Al, Na, Sb and Mo) by ICP-OES (PE2000, US), and the other half for the determination of 9 anions and cations (F^- , Cl^- , NO_3^- , SO_4^{2-} , Na^+ , NH_4^+ , K^+ , Ca^{2+} and Mg^{2+}) by IC (Dionex ICS1000, US). A small part of the quartz filter was used for carbon analysis with a thermal optical carbon analyzer (Sunset Lab, US). The remaining part of the quartz filter was used for polycyclic aromatic hydrocarbons (PAHs) measurements. For PAH analysis, soluble organic matter on quartz filters was extracted with dichloromethane, fractionated and cleaned up through a silica gel column, and finally concentrated to 0.5 ml. GC/MS (Agilent 6890/5973, US) was employed to determine the 16 EPA priority controlling PAHs. The description on quality control and quality assurance for chemical analysis could be seen elsewhere^[24,25].

2 Results and discussion

2.1 PM mass concentration

Totally, 210 PM samples (105 pairs of $PM_{2.5}/PM_{2.5-10}$) were taken during 2005–2007 with more samples collected in winter than in summer. PM mass concentrations were remarkably higher in winter than in summer. The average $PM_{2.5}$ level of all samples was $102 \mu g/m^3$, which is close to the results of He et al.^[7] and Wang et al.^[26], but about 1–12 times higher than the PM samples collected in other countries and regions ($38 \mu g/m^3$ in Hong Kong in 2003^[27], $32 \mu g/m^3$ in Ho Chi Ming City in 1996–1998^[28], 22.3 and $22.5 \mu g/m^3$ in Dahaka and Rajshahi, Bangladesh in 2001–2002^[29]). As for $PM_{2.5-10}$, a similar trend was observed. Average ratios of $PM_{2.5-10}$ to $PM_{2.5}$ ($PM_{2.5-10}/PM_{2.5}$) were calculated based on the data from pairs of $PM_{2.5-10}/PM_{2.5}$ samples. The mean ratio in summer is much lower (0.55) than in winter (0.70), and the annual average value is 0.62, close to Sillanpaa's study^[30]. Since it is humid in summer in Beijing, the conditions favor lower $PM_{2.5-10}$ concentrations (due to low re-suspension rate); while it is dry and windy in winter, favoring higher $PM_{2.5}$ and $PM_{2.5-10}$ concentrations (due to re-entrained dust and additional coal consumption for space-heating).

2.2 Characteristics of pollution elements

Enrichment factors (EF) were used to check possible contributions of non-crust sources based on our observed data (Figure 2). Here, aluminum was used as the reference element. We found that almost all the elements

Figure 2 Enrichment factors of elements in $PM_{2.5}$ and $PM_{2.5-10}$. CE, Crust elements; SPE, semi-pollution elements; PE, pollution elements.

had higher EF values in $PM_{2.5}$ than in $PM_{2.5-10}$, though these values varied from element to element. In $PM_{2.5}$, crust elements such as Ca, Ti, Fe, Mg and Sr were not significantly enriched as expected. Semi-pollution elements like Na, K, Mn, V and Mo, and some pollution elements such as Cr, Ni, Co, Cu and Sb were moderately enriched with EF less than 100 (dash line in Figure 2). Some pollution elements Se, Pb, Zn, As and Cd were highly enriched (EF > 100) due to the contribution of local anthropogenic sources such as coal combustion and vehicular emissions.

Obvious variations were observed in the ambient levels of elements (Figure 3). The levels of crust elements like Ca, Ti, Fe, Al, Mg and Sr and semi-pollution elements, such as K, V, Mn, Na and Mo, were higher in the coarse fraction $PM_{2.5-10}$. On the contrary, pollution elements, such as Cr, Ni, Co, Cd, Cu, Zn, Se, Pb, As and Sb, were found to be more abundant in the fine fraction $PM_{2.5}$. Semi-pollution elements like Na, K, V, Mn and Mo did not show obvious seasonal changes as compared with crust and pollution elements.

Figure 3 Seasonal variation of elements in $PM_{2.5}$ and $PM_{2.5-10}$ at the RCEES site.

The average ambient concentration of Pb reached $356 \text{ ng}/\text{m}^3$ in $PM_{2.5}$ in winter. This value was close to those reported in 1999–2000^[7,31] ($300 \text{ ng}/\text{m}^3$ and $335 \text{ ng}/\text{m}^3$), but was much higher than the level of $178 \text{ ng}/\text{m}^3$ reported by Sun et al. during 2001–2003 at the BNU urban site in Beijing^[32]. The Pb levels at our suburban site were also much higher than those in other Asian and European cities^[33–36]. It is curious to note that leaded gasoline has been prohibited since 1997 in Beijing. Consequently, there might be sources other than automobile exhausts. The background concentration of soil Pb in Beijing was reported to be $24.6 \text{ mg}/\text{kg}$ ^[37].

Another notable trace element is Se. The Se levels at the RCEES site ($41 \pm 40 \text{ ng}/\text{m}^3$) were higher than those

in other cities: $2 \text{ ng}/\text{m}^3$ in Urumuqi, $8.8 \text{ ng}/\text{m}^3$ in Lanzhou, $11 \text{ ng}/\text{m}^3$ in Chengdu, $13 \text{ ng}/\text{m}^3$ in Seoul, and $0.28 \text{ ng}/\text{m}^3$ in Okushiri Island^[38,39]. The possible sources of Se are as follows: (1) The Se abundance in the soil of the Beijing area is high^[40]. (2) Since coal is still used in the suburban areas of Beijing for cooking and space heating, emissions from coal combustion sources might contribute to the high Se levels in PM. (3) The soil in the nearby villages might be polluted by some non-agricultural activities, such as disassembly of discarded electronic equipment (computers, photocopiers and printers) as well as metal finishing.

The abnormal contents of Pb and Se led us to investigate the possible contribution of re-entrained contaminated soil particles from local disassembly activities. The results will be discussed in section 2.6 below.

2.3 Characteristics of ionic species

The most abundant inorganic ions in $PM_{2.5}$ and $PM_{2.5-10}$ were SO_4^{2-} and NO_3^- . Both of them gave remarkable values in winter and summer. The contributions of SO_4^{2-} and NO_3^- to total $PM_{2.5}$ mass were higher in summer (30.7% and 19.7%) than in winter (27.1% and 16.8%), and the absolute values of SO_4^{2-} and NO_3^- in $PM_{2.5}$ were 4 and 3 times of the average values in $PM_{2.5-10}$. The meteorological factors and high levels of O_3 made the secondary pollutants to be the main constituents of $PM_{2.5}$ in summer. The ratio of $\text{NO}_3^-/\text{SO}_4^{2-}$ can be considered as an indicator of the relative importance of vehicular emission vs. coal combustion in China^[41]. In our case, the average ratio of $\text{NO}_3^-/\text{SO}_4^{2-}$ is 0.65 in $PM_{2.5}$. Our ratio turned out to be larger than Yao's value of 0.58^[42], indicating an increasing contribution of NO_3^- . The contribution of vehicular emissions is becoming more important. However, as compared with the ratios in Arimoto's study^[43], our average ratio was not very high, and generally did not exceed 1. This implies coal combustion remained to be an important source of atmospheric particulate matters in the suburban and rural areas of Beijing, although coal has been substituted by natural gas for cooking and space heating in urban areas.

Ions other than SO_4^{2-} and NO_3^- also showed obvious characteristic seasonal variation. All the measured ions had higher levels in winter than in summer except NH_4^+ due to the relatively intensive photochemical reactions in summertime. The ion proportions in $PM_{2.5}$ obviously differed from those in $PM_{2.5-10}$. For instance, the percentages of Ca^{2+} were higher in $PM_{2.5-10}$ (in summer:

19.1% and in winter: 22.7%) than in PM_{2.5} (in summer: 2.63% and in winter: 2.53 %), as shown in Figure 4. The absolute values of Ca²⁺ in PM_{2.5-10} were 4 times higher than those in PM_{2.5}. Relatively high Ca²⁺ contents in PM_{2.5-10} might be associated with the intensive construction activities in Beijing in these years.

Figure 4 Main ion species in PM_{2.5} and PM_{2.5-10} at the RCEES site.

2.4 Characteristics of OC, EC and PAHs

The OC and EC levels in PM_{2.5} and PM_{2.5-10} showed a temporal variation (Table 1). In winter, OC/EC levels in PM_{2.5} were 37.1 and 6.36 μg/m³, and those levels in

Table 1 Seasonal variation of OC, EC and PAHs in PM_{2.5} and PM_{2.5-10} during the sampling period (OC and EC: μg/m³; PAHs: ng/m³)

	Summer		Winter	
	PM _{2.5}	PM _{2.5-10}	PM _{2.5}	PM _{2.5-10}
OC	20.47 ± 9.77	10.31 ± 6.11	37.1 ± 17.56	14.71 ± 6.86
EC	4.84 ± 3.83	3.3 ± 2.11	6.36 ± 5.65	4.06 ± 3.44
Na	0.23 ± 0.14	0.05 ± 0.02	0.54 ± 0.15	0.63 ± 0.07
Ace	0.05 ± 0.07	0.01 ± 0.01	0.89 ± 0.12	0.71 ± 0.35
Acy	0.02 ± 0.01	0.27 ± 0.03	0.05 ± 0.05	0.03 ± 0.01
Fl	0.03 ± 0.01	0.36 ± 0.22	0.71 ± 0.24	0.27 ± 0.05
Phe	1.04 ± 0.37	0.89 ± 0.65	25.8 ± 7.22	8.3 ± 1.24
An	0.36 ± 0.43	0.11 ± 0.14	4.32 ± 1.68	1.11 ± 0.20
Flu	4.3 ± 2.29	2.39 ± 1.38	59.11 ± 18.92	17.32 ± 3.29
Pyr	3.27 ± 2.14	2.59 ± 1.21	49.11 ± 16.7	13.57 ± 2.72
BaA	1.36 ± 0.07	1.14 ± 0.71	30.02 ± 8.71	8.93 ± 1.07
Chr	3.77 ± 0.11	2.14 ± 0.81	44.38 ± 13.76	10 ± 1.40
BbF	5.25 ± 0.22	2.04 ± 0.60	33.84 ± 10.49	8.13 ± 3.23
BkF	3.86 ± 0.38	1.77 ± 0.44	19.29 ± 5.97	10.63 ± 2.18
BaP	1.19 ± 0.52	1.14 ± 0.67	19.82 ± 5.95	5.09 ± 0.81
InP	5.38 ± 0.53	2.84 ± 1.22	22.32 ± 6.92	6.25 ± 0.63
DbA	2.44 ± 0.60	2.84 ± 0.53	22.21 ± 7.55	4.43 ± 0.45
BghiP	6.96 ± 0.58	4.34 ± 0.59	28.84 ± 8.94	7.89 ± 0.79
ΣPAHs	39.52 ± 8.47	24.92 ± 9.17	361.24 ± 113.37	98.2 ± 18.49

PM_{2.5-10} were 14.71 and 4.06 μg/m³, respectively. On the other hand, OC/EC levels in summer were 20.47 and 4.84 μg/m³ for PM_{2.5}, and 10.31 and 3.3 μg/m³ for PM_{2.5-10}. OC had an increment in winter of 1.8 and 1.4 times in PM_{2.5} and PM_{2.5-10}, respectively; whereas EC in winter had an increment of 1.3 and 1.2 times in PM_{2.5} and PM_{2.5-10}, respectively. The OC contribution to the total mass of PM_{2.5} was in the range of 9%–50%, with an average of 32% in winter and 21% in summer. The EC contribution to PM_{2.5} was averagely 5% in both seasons. These figures are close to the results in an earlier study^[7].

OC vs. EC in PM_{2.5} and PM_{2.5-10} showed a good relationship with *R* = 0.78 and *R* = 0.90, respectively. This implies that OC and EC have the same origin. Usually, the ratio of OC/EC is used to confirm the existence of secondary organic aerosol^[44]. In the present study, the average ratios of OC/EC in PM_{2.5} and PM_{2.5-10} were 3.6 and 2.9, respectively. They were far beyond the recommended value 2.2^[44] for the recognition of secondary organic aerosol formation in both seasons.

The total PAH concentrations (sum of the 16 EPA priority pollutants) in 60 samples ranged from 2.1 to 754 ng/m³, with mean values of 199.23 and 64.06 ng/m³ for PM_{2.5} and PM_{2.5-10}, respectively. The highest PAH levels were found in winter in PM_{2.5} (754.04 ng/m³), and the total levels of 16 PAHs in winter were 1.3–38.6 times higher than those in summer. Although the ratio of total PAHs in winter to that in summer was similar to the ratio in Hong Kong at a traffic site^[45], the total 16 PAHs concentration in this study was much higher than that in Hong Kong^[46] (27.93 ng/m³), and was about 100 times higher than that in Houston, US^[9].

Furthermore, the average benzo[a]pyrene concentration was 10.04 ng/m³. It exceeds the allowable concentration of 1 ng/m³ recommended by WHO, and is also higher than the BaP levels in other cities^[9,46]. For PM_{2.5}, the average proportions of PAH species were in the following descending order: four rings (49.85%) > five rings (28.86%) > six rings (13.26%) > three rings (7.83%) > two rings (0.19%). The PAH species in PM_{2.5-10} had the same trend. Since the two- and three-ring PAHs were volatile and apt to degrade due to the higher temperature and stronger sunlight in summer, their concentrations were rather low in comparison with four- or six-ring PAHs.

Molecular indices based on ratios of concentrations of

selected PAH species are useful to differentiate PAHs from different sources. Phe/An and Phe/(Phe+An) are considered as indicators of combustion sources. The values of Phe/(Phe+An) of 0.5, 0.65 and 0.76 were indicative of the contribution of emissions from gasoline engines, diesel engines and coal combustion, respectively^[47]. In our case, the ratio of Phe/(Phe+An) in PM_{2.5} was 0.85. The ratio of Phe/An was found to be 5.74, which is close to Napples' result —5.5^[48]. A recent report^[49] suggested that the ratios for coal combustion vary in a wide range of 3–70.2, depending on the different kinds of coal used. From the above data, we can conclude that at the RCEES site coal combustion in winter was an important source of PAHs. In fact, our survey in the Bajia villages confirmed coal was still in use. Bap/BghiP is usually used to characterize vehicular fuel emissions. We obtained a moderate value of 0.59 for PM_{2.5}. It falls in the range of 0.3–0.78 for mobile sources^[47], suggesting that the vehicle emissions were also important. The ratio of BaA/Chr was found to be 0.69, which is also close to the ratio of 0.63 for mobile sources^[47].

2.5 Source apportionment

The PMF (positive matrix factorization) software was employed for the study of source apportionment. This approach is highlighted by the appropriate error estimation and non-negativity of the resulting factors^[50]. The 2-way model in the PMF package was applied to our datasets. Before computation, all input data were normalized to a basis of 24 h. Missing values were substituted by the mean of measured values; and data below

detection limits (BDL) were replaced by one half of the detection limit of the species^[21]. After data processing, 21 chemical species (F^- , Cl^- , NO_3^- , SO_4^{2-} , NH_4^+ , K, Na, Mg, Al, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Sr and Pb) were employed for PM_{2.5} and PM_{2.5-10} apportionment.

The PMF model ran with various parameter values until the most physically reasonable results were obtained. In case of PM_{2.5}, the results given by 8 factors were the most reasonable, and about 95% of the data can be explained by these 8 factors. For PM_{2.5-10}, the results with 5 factors were the easiest for interpretation, and 91% can be explained (Figure 5). Among these resolved factors, 5 types of sources are common to both fine and coarse particles:

Source 1 represents the local soil-related sources with typical crust elements, i.e., Mn, Mg, Ca, and Ti, including soil particles and fugitive dust. This is an important source of Beijing aerosol.

Source 2 is dominated by K^+ , representing the source of biomass combustion emissions. It includes most likely agricultural residues and firewood burning.

Source 3 is represented by Al and Fe. Besides the contribution from soil, these elements might also come from local metal working, since there were many small courtyard and curbside metal workshops, where metal welding and cutting were carried out in the open space.

Source 4 is rich in Zn, Pb and Cu. Zn possibly came from fuel combustion or tyre abrasion, and other researchers have proved the existence of Zn in vehicle exhausts^[51]. It was used as the fingerprint of mobile vehicle emission sources in recent PMF analysis^[52]. Pb might stem from the minute amounts of lead additive in

Figure 5 Source apportionment for PM_{2.5} (left) and PM_{2.5-10} (right) at the RCEES site. BB, Biomass burning; CC, coal combustion; Metal, manufacture activities; RD, road dust; SI, secondary ions; SP, soil particulate; VE, vehicle emissions; UN, unidentified source associated with F; Others, sources not resolved by PMF.

the gasoline produced by the out-of-dated refineries in China after leaded-gasoline was banned in 1997. Cu might come from the sampling pump or from the braking system^[53]. We ascribe source 4 as the mobile source. Source 5 is characterized by F^- in both $PM_{2.5}$ and $PM_{2.5-10}$. During our PMF computation, no matter how the parameters were altered, F^- always showed rather high values both for $PM_{2.5}$ and $PM_{2.5-10}$. It needs further investigation.

Besides these five common sources mentioned above, there are other specific sources for $PM_{2.5}$, namely, coal combustion source characterized by As, Cl^- , and SO_4^{2-} ; road dust characterized by Ni, Cr, Na and Mg; and secondary particles represented by NO_3^- , SO_4^{2-} and NH_4^+ .

For the quantitative estimation of mass contributions of these resolved factors, the observed PM mass concentrations were regressed against the factor scores using multi-linear regression (MLR). And the average source contributions of each factor to the total mass were derived from this regression process. The annual arithmetic means of the total mass apportionment for different types of sources at this site are shown in Figure 5. We found that secondary particles were the largest contributor for $PM_{2.5}$ accounting for about 28%, while the soil-related source was the predominated contributor for $PM_{2.5-10}$ with a percentage of 49%. From the source apportionment results, we could see that fine particles ($PM_{2.5}$) have distinct anthropogenic feature, and man-related activities such as fuel combustion vehicle emission is the main contributors. While, for coarse particles ($PM_{2.5-10}$), more local sources-local soils and fugitive dust is characterized. This difference could be explained by their difference formation mechanism.

2.6 Tracking potential source of Pb and Se

As mentioned above, the Pb and Se levels in particulate samples at this site were relatively high, reminding the possible presence of small sources of these elements. In order to find the local potential sources, we made some preliminary survey in the upwind direction of our sampling site. The nearest small potential sources could be the Front Bajia and Back Bajia villages, where thousands of tenants earned their living by collecting and disassembling discarded electronic equipment and undertaking metal finishing business. The contents of pollution elements (Pb, Se, Zn, Cu, Ni, Cd, Co, Cr, As and Sb) in the soil samples and in dust sample collected at 8 points (Figure 1) surrounding our air PM sampling site

were determined as shown in Table 2. The soil sample taken from the electronic waste disassembly site had the highest contents among the soil samples.

The parameter of CD (coefficient of divergence) was used to judge the similarity or difference in the concentrations of various chemical elements in soil samples from different sampling sites^[54]. CD can be defined as

$$CD_{jk} = \sqrt{\frac{1}{p} \sum_{i=1}^p \left(\frac{x_{ij} - x_{ik}}{x_{ij} + x_{ik}} \right)^2},$$

where x_{ij} represents the average concentration of a pollution element i at site j , j and k represent a pair of sampling sites in comparison, and p is the number of pollution elements. If the CD value approaches zero, the data from the two sites are considered to be similar. If the CD value approaches unity, they are considered to be significantly different.

Mean concentrations of the pollution elements Pb and Se in soil samples from 7 sampling points and one rooftop dust sample (shown in Table 2) were employed in the CD calculation. Figure 6 evidently shows three clusters of CD values. All CD values associated with the obsolete electronic equipment disassembly site are larger and lie in the upper part of the figure, whereas those associated with other 6 soil sampling sites are smaller and lie in the lower part of Figure 6. Those associated with the dust sample are marked with a circle in Figure 6, lying in the middle. Segregation of the CD values implies that the chemical feature of soil at the electronic equipment disassembly site was different from those at other soil sampling sites irrespective to their spatial locations. Activities linked with disassembly of computers, printers, TV, CRT and CD players might result in more serious contamination of soil by Pb, Se, Zn, Cu and Ni. Since these elements were also detected in the dust sample with medium CD values, these activities might also be a source of atmospheric particles and their impacts should not be ignored.

The pollution problem in Bajia will be solved in the near future, as these poor quarters in Bajia will be demolished according to the municipal development plan, and our long-term monitoring will evidence the growth and decline of these typical anthropogenic area sources in Beijing. Nevertheless, the pollution issue associated with electronic wastes will remain in China and should not be overlooked, as more than 70% of the global electronic wastes are transported to China^[55].

Table 2 Pollution element contents in soil and dust samples (mg/kg)

Sites		A	B	C	D	E	F	G	H	Background
As	Mean	72.83	54.67	80.00	58.41	41.16	63.16	9.38	48.00	7.09 ^[37]
	SD	14.13	9.24	6.73	8.55	12.36	9.88	4.86	12.23	
Cd	Mean	47.94	32	40.87	30.48	27.25	33.68	30	34.18	0.12 ^[37]
	SD	0.09	0.07	0.08	0.03	0.08	0.04	0.07	0.09	
Co	Mean	129.06	84	106.09	79.37	72.46	89.12	81.25	90.91	–
	SD	0.21	0.05	0.27	0.18	4.02	0.26	0.23	0.25	
Cr	Mean	238.76	117.33	139.13	81.9	115.36	127.72	118.13	182.55	29.8 ^[37]
	SD	0.3	0.25	0.35	0.23	0.11	0.77	0.2	0.51	
Cu	Mean	187.14	604.67	88.7	70.48	86.38	110.88	275	101.09	18.7 ^[37]
	SD	0.69	2.95	0.4	0.07	0.31	0.28	0.85	0.21	
Ni	Mean	148.42	284	106.09	72.38	78.84	96.84	92.5	96.73	26.8 ^[37]
	SD	0.5	1.23	0.26	0.27	0.39	0.53	0.19	0.36	
Pb	Mean	473.84	1480	93.91	80.63	101.45	120	255.63	122.91	24.6 ^[37]
	SD	3.65	26.19	2.59	1.15	1.52	1.08	0.49	1.79	
Sb	Mean	84.81	77.33	73.04	55.24	48.7	61.75	63.13	61.82	–
	SD	2.75	1.5	1.68	1.57	2.15	1.08	3.43	1.31	
Se	Mean	40.56	64.67	47.83	32.38	29.57	40.7	24.38	38.55	0.24 ^[40]
	SD	3.54	10.25	9.56	3.83	5.2	6.19	4.44	5.09	
Zn	Mean	717.22	2192	154.78	187.3	251.01	407.72	275.18	253.09	57.5 ^[37]
	SD	2.21	8.28	0.33	0.67	1.89	1.91	1.44	2.78	

A, Dust from the rooftop of a RCEES building; B, soil in the yard of an electronics disassembling shop; C, soil in the campus of Beijing Forestry University; D, soil in front of a waste recycling point; E, soil from a waste disposal station; F, soil in front of a small restaurant; G, soil in front of a curbside waste collection site; H, soil in front of a curbside metal workshop.

Figure 6 The CD values for Pb and Se in soil samples at different locations. A, Dust from the rooftop of the RCEES PM sampling site; B, soil in the yard of an electronics disassembling shop; C, soil in the campus of Beijing Forestry University; D, soil in front of a waste recycling point; E, soil from a waste disposal station; F, soil in front of a small restaurant; G, soil in front of a curbside waste collection site; H, soil in front of a curbside metal workshop.

3 Conclusion

Elemental analysis indicated that crust elements (Al, Ca, Mg, Fe, etc.) were abundant in the coarse mode and pollution elements such as Pb, Sb, Se, As, and Cd were highly enriched in the fine mode. The Pb levels, never-

theless, remained high in both modes after phasing-out leaded gasoline since 1997. SO_4^{2-} , NO_3^- and NH_4^+ were the main ions in $\text{PM}_{2.5}$, whereas SO_4^{2-} , NO_3^- and Ca^{2+} dominated in $\text{PM}_{2.5-10}$. Total concentrations of OC+EC were higher in winter, which averagely accounted for about 31% and 24% in $\text{PM}_{2.5}$ and $\text{PM}_{2.5-10}$, respectively. The ratios of OC/EC in both modes suggest the wide existence of secondary organic aerosols in Beijing. The GC/MS results show relatively high PAH levels in Beijing in wintertime related to the coal burning and emission of mobile vehicles.

Source apportionment results indicated that secondary particulate matters were the main sources of fine particulate matters, and the sources of coarse particulate matters were dominated by the soil-related particulate matters.

Tracking potential local sources of air particulate matters led us to identify courtyard electronics disassembly activities in Bajia villages as an area source of heavy metals. The environmental impacts of these emerging activities in the juncture belt of big cities should not be overlooked.

Long-term monitoring and source apportionment after phasing-out leaded gasoline has the advantage of tracking emerging overlooked sources.

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