Size distributions and sources of elements in particulate matter at curbside, urban and rural sites in Beijing

Jingchun Duan[1], Jihua Tan[2], Shulan Wang[1], Jimin Hao[3], Fahe Chai[1,*]

1. State Key Laboratory of Environmental Criteria and Risk Assessment, Chinese Research Academy of Environmental Sciences, Beijing 100012, China. E-mail: duanjc@craes.org.cn
2. Key Laboratory of Computational Geodynamics, Graduate University of the Chinese Academy of Sciences, Beijing 100049, China
3. School of Environment, Tsinghua University, Beijing 100084, China

Abstract

Size distributions of 29 elements in aerosols collected at urban, rural and curbside sites in Beijing were studied. High levels of Mn, Ni, As, Cd and Pb indicate the pollution of toxic heavy metals cannot be neglected in Beijing. Principal component analysis (PCA) indicates 4 sources of combustion emission, crust related sources, traffic related sources and volatile species from coal combustion. The elements can be roughly divided into 3 groups by size distribution and enrichment factors method (EFs). Group 1 elements are crust related and mainly found within coarse mode including Al, Mg, Ca, Sc, Ti, Fe, Sr, Zr and Ba; Group 2 elements are fossil fuel related and mostly concentrated in accumulation mode including S, As, Se, Ag, Cd, Tl and Pb; Group 3 elements are multi-source related and show multi-mode distribution including Be, Na, K, Cr, Mn, Co, Ni, Cu, Zn, Ga, Mo, Sn and Sb. The EFs of Be, S, Cr, Co, Ni, Cu, Ga, Se, Mo, Ag, Cd, Sb, Tl and Pb show higher values in winter than in summer indicating sources of coal combustion for heating in winter. The abundance of Cu and Sb in coarse mode is about 2–6 times higher at curbside site than at urban site indicating their traffic sources. Coal burning may be the major source of Pb in Beijing since the phase out of leaded gasoline, as the EFs of Pb are comparable at both urban and curbside sites, and about two times higher in winter than that in summer.

Key words: ELPI; enrichment factor; curbside; atmosphere; heavy metal

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Introduction

Elements are released to the atmosphere from both anthropogenic and natural sources. Anthropogenic sources include fossil fuel combustion, industrial metallurgical processes, vehicle emission and waste incinerations. Natural sources include a variety of processes acting on crustal minerals, such as volcanism, erosion and surface winds, as well as from forest fires and the oceans. Some elements are potentially toxic trace metals, such as Pb, Cd, V, Fe, Zn, Cr, Ni, Mn and Cu. Studies show that metals associated with ambient particles catalyze oxidative stress (Ghio et al., 1999; Muránszky et al., 2011), and may be responsible for production and release of inflammatory mediators by the respiratory tract epithelium, which contribute to the toxic effects of particulate air pollutants reported in epidemiological studies (Carter et al., 1997).

Knowledge of the size distribution of particulate matter (PM) is not only vital in understanding its effects on human health, its sources and source processes and transformation processes during atmospheric transport, but also for estimation the dry deposition of the aerosol (Trijonis 1983; Pakkanen et al., 2001; Salma et al., 2005; Duan et al., 2007; Tan et al., 2009). The size distribution of elements

within atmospheric particles has been studied over cities around the world, such as Kanazawa, Japan (Wang et al., 2006), Helsinki, Finland (Pakkanen et al., 2001) and Los Angeles, USA (Singh et al., 2002). Beijing is the capital of China with a population of over 15.81 million. Serious air pollution has been reported in Beijing, and coal burning, vehicle emission, secondary aerosol, Asian dust, biomass open burning and crust soil have been reported responsible for the situation (Mori et al., 2003; Sun et al., 2004; Wang et al., 2005; Duan et al., 2008). Elements in Beijing have been studied, and several methods have been used for source identification and apportionment including factor analysis (FA) and chemical mass balance (CMB) (Sun et al., 2004; Okuda et al., 2004). However, few researches on size distribution of elements in aerosol have been carried out in Beijing (Ning et al., 1996), particularly for aerosol down to ultrafine fraction.

1 Experimental

1.1 Study area and sampling

A 13-stage low pressure impactor (LPI, Dekati, Tampere, Finland) was used to provide resolution of the size distribution of aerosol populations from coarse particles to ultrafine particles. PTFE filter substrates (Pall Corporation,

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* Corresponding author. E-mail: chaifh@craes.org.cn

Michigan, USA) were used on all stages, and at a flow rate of 10 L/min the 50% cut off diameters (D_{50}, μm) were 9.92, 6.68, 4.00, 2.39, 1.60, 0.948, 0.613, 0.382, 0.263, 0.157, 0.095, 0.056 and 0.028.

As shown in Fig. 1, Tsinghua site is an urban site on the rooftop of a building (5 m above the ground) within Tsinghua University, which is located 20 km in the northwest direction from the center of Beijing and 2 km from 4th Ring Road. Some boilers for heating and cooking may exist in the vicinity. The 4th Ring site is a curbside site on an overpass above 4th Ring Road which is a major artery around the centre of Beijing, carrying 220,000 vehicles per day in eight main lanes and six auxiliary lanes. Miyun site is a rural site on top of a little hill about 60 km in the northeast direction from urban Beijing. There are no obvious aerosol sources at Miyun site, except for a railway line about 100 m away.

Samples with duration ranges from 48–72 hr were collected at the three sites in both winter and summer except a sampling failure in summer at Miyun site, and the conditions during sampling periods are listed in Table 1. Since the sampling at the three sites was not conducted concurrently and the amount of collected aerosol depends strongly on the weather conditions, spatial variations should be discussed carefully.

1.2 Chemical analysis

The aerosol-loaded filters were placed in Teflon tubes with a 4-mL mixture of concentrated hydrochloric acid and nitric acid at volume ratio of 3:1, and then microwaved for 58

Fig. 1   Location of the three sampling sites in the city of Beijing.

Table 1   Conditions during sampling periods

Location	Date	Temperature	Averaged RH
Tsinghua (winter)	Jan 13–Jan 15, 2006	–8~0°C	77%
4th Ring (winter)	Jan 20–Jan 22, 2006	–8~0°C	57%
Miyun (winter)	Feb 17–Feb 20, 2006	–7~12°C	21%
Tsinghua (summer)	Jun 8–Jun 12, 2006	15~33°C	42%
4th Ring (summer)	Jun17–Jun 20, 2006	18~37°C	35%

RH: relative humidity.

min to ensure the complete digestion of particles collected on Teflon filters. The microwave process consisted of four steps under the operation power of 1200 W. The first step is to have temperature ramping to 120°C from room temperature in 5 min and holding for 5 min; the second is ramping to 155°C in 8 min and holding for 8 min; the third is ramping to 180°C in 5 min and holding for 5 min; and the last step is ramping to 195°C and holding for 12 min. Then, the digested solution was diluted to 10 mL using ultra-pure water (specific resistance ⩾18.3 MΩ·cm) to perform the metal analysis by inductively coupled plasma-mass spectrometry (ICP-MS) (Thermo, X serial) and ICP-AES (Thermo, IRIS Intrepid II XSP). The calibration was made using multi-element (metal) standards (certified reference materials (CRMs); National Analysis Center for Iron and Steel, China) in a 3% (V/V) HNO$_3$ solution.

Six blank filters were treated and analyzed in the same way as for the actual samples. In addition, the approximate detection limits (three times the standard deviation of blanks analyzed) were Al (76 ppb), Be (0.009 ppb), Na (39 ppb), Mg (50 ppb), S (47 ppb), K (27 ppb), Ca (243 ppb), Sc (0.78 ppb), Ti (3.16 ppb), Cr (6.20 ppb), Mn (1.50 ppb), Fe (108 ppb), Co (0.08 ppb), Ni (0.5 ppb), Cu (1.47 ppb), Zn (10 ppb), Ga (0.10 ppb), As (0.38 ppb), Se (0.83 ppb), Sr (0.51 ppb), Zr (0.41 ppb), Mo (0.18 ppb), Ag (0.05 ppb), Cd (0.03 ppb), Sn (0.33 ppb), Sb (0.33 ppb), Ba (1.75 ppb), Tl (0.006 ppb) and Pb (5.88 ppb).

2 Results and discussion

2.1 PM and element concentrations and PCA analysis

Concentrations of PM and elements are listed in Table 2. Some epidemiological evidences suggest mortality in urban areas may be linked to PM$_{10}$ (Lippmann, 1998). As shown in Table 2, the particle loadings at urban site (Tsinghua) and curbside (4th Ring) in winter were 184.9 and 210.9 μg/m^3 respectively, much higher than the National Ambient Air Quality Standard (NAAQS) of USA for PM$_{10}$ (150 μg/m^3 over a 24-hr period). The level was comparable with that of India cities (100–400 μg/m^3), however, was much higher than that reported in Western Europe and North America (10–55 μg/m^3) (Sharma and Mallo, 2005). The particle loading at rural site (Miyun) in winter was 58.1 μg/m^3, much lower than those at urban and curbside sites and below NAAQS for PM$_{10}$. Compared with those in winter, the particle loadings of 74.4 and 119.9 μg/m^3, respectively at Tsinghua and 4th Ring sites in summer were rather low and below NAAQS for PM$_{10}$.

Based on concentrations, the elements are divided into three groups: major elements (Al, Na, Mg, S, K, Ca and Fe, ⩾10^3 ng/m^3), sub-major elements (Ti, Cr, Mn, Ni, Cu, Zn, As, Sr, Sb, Ba and Pb, in the range of 10^1–10^3 ng/m^3), and minor metals (Be, Sc, Co, Ga, Se, Zr, Mo, Ag, Cd, Sn and Tl, ⩽ 10 ng/m^3). Of the major elements, Al, Na, Mg, K, Ca and Fe have similar levels at urban and curbside sites during both summer and winter. These elements should be mostly from soil dust. The concentration of S in winter was about 5 times higher
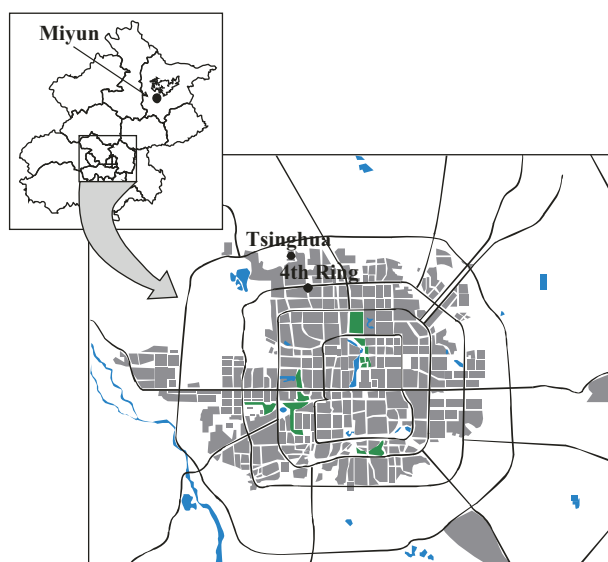
Table 2   Concentrations of elements and PM in Beijing

PM and trace elements	Tsinghua		4th Ring		Miyun	
	Winter	Summer	Winter	Summer	Winter	Summer
PM[a] (μg/m^3)	184.9	74.4	210.9	119.9	58.1	–[c]
Al (ng/m^3)	2181.8	3088.4	3007.3	5143.8	2181.8	–
Be (ng/m^3)	0.4	0.1	0.4	<dl[b]	0.1	–
Na (ng/m^3)	987.2	572.3	1977.6	952.1	1449.8	–
Mg (ng/m^3)	576.1	821.6	990.5	1637.2	637.0	–
S (ng/m^3)	9690.2	2147.5	10043.9	1983.1	2007.2	–
K (ng/m^3)	2555.8	1970.5	4091.6	3247.6	1170.3	–
Ca (ng/m^3)	1816.4	2441.2	3608.5	7484.3	996.9	–
Sc (ng/m^3)	<dl	0.5	1.4	0.9	<dl	–
Ti (ng/m^3)	117.5	174.6	179.7	300.5	69.4	–
Cr (ng/m^3)	178.4	13.2	22.4	72.9	21.8	–
Mn (ng/m^3)	112.8	66.3	128.5	102.4	35.6	–
Fe (ng/m^3)	2901.7	2188.7	4480.1	4106.7	1088.8	–
Co (ng/m^3)	2.9	1.0	2.4	1.7	0.6	–
Ni (ng/m^3)	89.0	16.6	25.0	19.4	20.2	–
Cu (ng/m^3)	55.1	20.0	80.3	77.2	10.0	–
Zn (ng/m^3)	317.6	187.5	469.5	430.6	27.8	–
Ga (ng/m^3)	15.0	4.2	20.9	9.5	2.7	–
As (ng/m^3)	21.9	–	22.3	–	2.9	–
Se (ng/m^3)	10.1	2.0	7.1	1.8	1.1	–
Sr (ng/m^3)	22.9	10.3	38.2	25.0	9.8	–
Zr (ng/m^3)	6.6	5.5	13.5	18.3	1.9	–
Mo (ng/m^3)	28.7	1.7	11.9	7.8	6.5	–
Ag (ng/m^3)	1.5	0.4	1.2	0.2	0.1	–
Cd (ng/m^3)	4.2	1.0	3.6	1.1	1.1	–
Sn (ng/m^3)	13.4	6.0	19.4	8.7	1.8	–
Sb (ng/m^3)	17.9	5.3	23.2	16.3	0.6	–
Ba (ng/m^3)	34.5	34.1	118.9	96.5	18.4	–
Tl (ng/m^3)	2.1	0.6	1.6	0.5	0.2	–
Pb (ng/m^3)	468.2	90.1	323.9	64.9	52.9	–

[a] In this study, PM range from 0.028 to 9.92 μm; [b] under detection limit; [c] not determined.

than that in summer at urban and curbside sites. This should be the result of coal burning for heating in winter in Beijing. Although with low concentrations, most sub-major and minor elements are toxic. However, of them, the Ministry of Environmental Protection of the People's Republic of China has a NAAQS only for Pb and just includes some toxic heavy metals in NAAQS (draft in comment). As shown in Tables 2 and 3, the levels of Pb (52.9–468.2 ng/m^3), Cd (1.0 and 4.2 ng/m^3) and Mn (35.6–128.5 ng/m^3) are approaching NAAQS (draft in comment) and World Health Organization (WHO) guidelines (WHO, 2000b) at urban sites in winter; the levels of As (2.9–22.3 ng/m^3) and Ni (16.6–89.0 ng/m^3) high enough that the levels exceed NAAQS (draft in comment) and WHO guidelines in most of the sampling periods. It indicates the pollution of toxic heavy metals in Beijing cannot be neglected.

Five sets of total 60 samples were used to evaluate the possible dominant emission sources by principal component analysis (PCA) in Beijing. As shown in Table 4, four possible sources were identified. PC1 is heavily loaded with mass, Be, S, K, Mn, Cu, Zn, Ga, Se, Ag, Cd, Sn, Sb, Tl and Pb. It indicates combustion sources, since S, Se are typically coal combustion related, K may be biomass combustion related and Mn, Cu, Zn, Cd, Sn are related to vehicle emissions (Lin et al., 2006 and references therein). PC2 is heavily loaded with Al, Mg, Ca, Ti, Mn, Fe, Co, Cu, Sr, Zr, and Ba. It indicates crust related sources (Trapp et al., 2010). PC3 is heavily loaded with Cr, Ni and Mo.

Table 3   Comparison of levels of some toxic elements with NAAQS in China and WHO guidelines (unit: ng/m^3)

Toxic elements	This study	NAAQS	NAAQS (draft in comment)[a]	WHO
V	–	–	1000	1000
Cr	13.2–178.4		0.025 (Cr(VI))	0.25 (Cr(VI))[b]
Mn	35.6–128.5	–	150	150
Ni	16.6–89.0	–	20	25 [b]
As	2.9–22.3	–	6	6.6 [b]
Cd	1.0-4.2	–	5	5
Hg	–	–	1000	1000
Pb	52.9–468.2	1000	500	500

[a] http://www.mep.gov.cn/gkml/hbb/bgth/201011/t20101130_198128.htm;
[b] concentrations corresponding to an excess lifetime risk of 1:100,000.

It indicates traffic related sources as discussion in Section 2.2. PC4 is loaded with Be, Ga and Tl. Since Be, Ga and Tl are all volatile and exist also in PC1, PC4 should be related to coal combustion and volatile species.

2.2 Size distribution of elements

The elements can be roughly divided into three groups based on particle size distribution. The Group 1 elements are mostly concentrated in coarse mode including Al, Mg, Ca, Sc, Ti, Fe, Sr, Zr and Ba; the Group 2 elements are mostly concentrated in accumulation mode including S, As, Se, Ag, Cd, Tl and Pb; The group 3 elements have muti-mode distribution including Be, Na, K, Cr, Mn, Co, Ni, Cu, Zn, Ga, Mo, Sn and Sb. Given the similarity at the three sampling sites, size distributions of elements at

Tsinghua site are shown in Fig. 2.

Enrichment factors (EFs) of elements in aerosol are employed to assess the extent of non-crustal contributions to the elemental concentration levels for the three groups. The EF_{Crust} of element E in aerosols is defined as below (Wang et al., 2006):

$$EF_{Crust} = (E/R)_{Air}/(E/R)_{Crust} \qquad (1)$$

where, R is a reference element of crustal material, $(E/R)_{Air}$ is the concentration ratio of E to R in aerosol sample, and $(E/R)_{Crust}$ is the concentration ratio of E to R in the
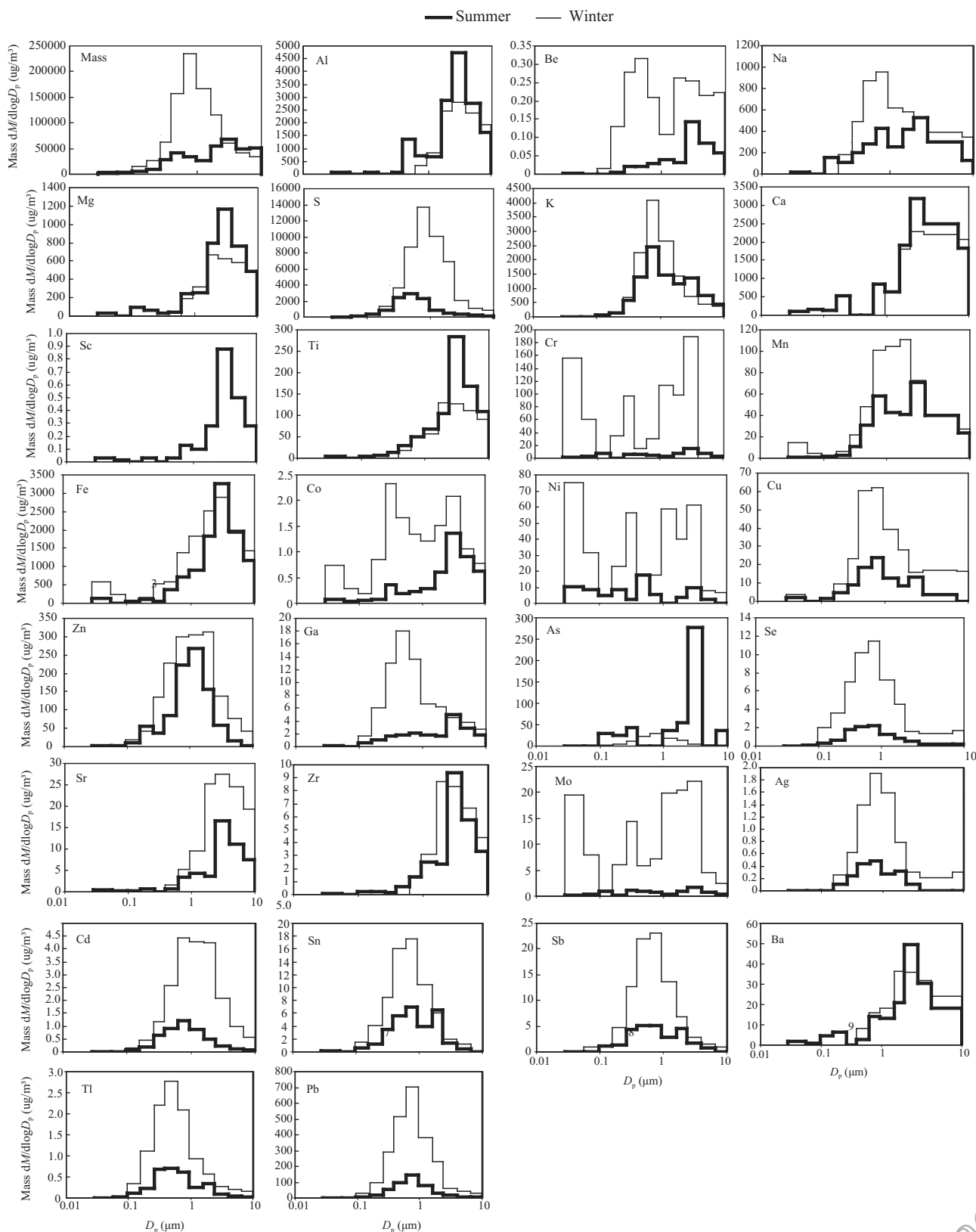

Fig. 2 Size distribution of PM and elements at Tsinghua site in Beijing.

Table 4 Factor analysis for mass and elements in Beijing

Compound	Factor			
	PC1	PC2	PC3	PC4
Mass	0.85	0.42		
Al		0.94		
Be	0.49	0.62		0.48
Mg		0.96		
S	0.97			
K	0.87			
Ca		0.96		
Ti		0.97		
Cr			0.96	
Mn	0.61	0.72		
Fe		0.97		
Co		0.72	0.40	
Ni			0.96	
Cu	0.58	0.72		
Zn	0.79			
Ga	0.75	0.43		0.45
Se	0.92			
Sr		0.92		
Zr		0.96		
Mo			0.93	
Ag	0.95			
Cd	0.89			
Sn	0.94			
Sb	0.78	0.48		
Ba		0.94		
Tl	0.82			0.48
Pb	0.95			
Initial eigenvalue	13.85	7.36	2.73	1.01
Variance (%)	51.30	27.27	10.12	3.74
Cumulative (%)	51.30	78.58	88.69	92.43

Extraction method: principal component analysis. Rotation method: Varimax with Kaiser normalization. Only factor loadings ⩾ 0.4 listed. Only factors with eigenvalue ⩾ 1 shown. Source apportionment method: PCA.

crust. There is no widely accepted rule for the choice of the reference element; however, Si, Al and Fe are usually used for this purpose. In this study, Fe is used as the reference element and the abundance of elements in the upper continental crust (UCC) is taken from previous publication (Taylor and McLennan, 1985).

As shown in Fig. 3, the EFs for Group 1 element are in the range of 0.33–2.09 for coarse mode particles and 0.10–2.56 for accumulation mode particles. It indicates these elements are mostly crust related. Ca can also be from construction dust in Beijing. Zhang and Iwasaka (1999) found Ca abundant particles with little or no other mineral elements existed in their samples collected during five dust storms in the spring of 1995 and 1996. They concluded that Ca abundant particles originated from local construction activities. He et al. (2001) found Ca/Si and Ca/Al ratios were the lowest in winter when construction activity decreased. In this study, the Ca/Al ratio ranked in the order of 4th Ring curbside (1.20–1.46) > Tsinghua urban site (0.79–0.83)> Miyun rural site (0.46). There is no distinct seasonal variation observed, however, high Ca/Al ratios at curbside and urban sites indicate anthropogenic sources such as construction activities.

The EFs for Group 2 element are in the range of 0.8–700 for coarse mode particles and 50–6325 for accumulation mode particles. High value of EFs in accumulation mode indicates these elements should be related to coal combustion and vehicle emission. Relatively high EFs in coarse mode of most Group 2 elements than those of Group 1 indicate they should mainly come from the re-suspended soil containing previously deposited PM. The highest EFs for Group 2 are that of Se (range: 2483–6325). Se is a marker for coal combustion, and the average abundance of Se in Chinese coal (Zhao et al., 2002) is about 400 times of that of UCC. In recent years, coal combustion consumption has reached to 30 million tons per year in Beijing. The mode of Se shifts a little to smaller size compared with that of mass, which is similar to that found for semi-volatile PAHs (Duan et al., 2005). It was reported that Se is volatile, and Se would mostly be in the gas phase and fly ashes after combustion (Yan et al., 2001). Gas phase Se would be adsorbed on the surface of particles after emission, and the mode of surface area generally shift a little to smaller size than the mode of mass. Similar characteristics are also found for elements Ga (in winter), Sn (in winter) and Tl. Ag, As and Cd may also be emitted from coal combustion since their abundances in Chinese coal are 10, 3.3 and 2 times of those of UCC and may be greatly elevated after combustion.

The EFs for some elements of Group 3 such as Be, Na, K, Mn, Co are less than 10 in both coarse mode and accumulation mode particles. For coarse mode, these elements may come from crust soil; however, for accumulation mode, these elements may come from fossil fuel combustion and vehicle emission. Compared with other fossil fuel related metals, Mn and Co have relatively lower EFs. The reason may be that Mn and Co are hardly vaporized during coal combustion and are equally distributed between bottom ashes and fly ashes (Yan et al., 2001), therefore in flue gas the EFs are much lowered. The EFs of Cu, Zn, Mo and Sb of 43-2947 in accumulation mode and 4.3–513 in coarse mode suggest these elements come from fossil fuel combustion and the re-suspended soil containing previously deposited PM. The EFs of Cr, Ga and Sn of of 7–92 in accumulation mode and 2.8–34 in coarse mode indicate their sources are both anthropogenic activities and crust soil. The ultra-fine mode for Cr, Co, Ni and Mo may indicate diesel emission, since diesel engine emits high concentrated ultra-fine particles and high concentration for these metals was found in diesel emission (Kittelson et al., 2004; Wang et al., 2003). Similar multi-mode distribution was also found for Cr and Ni at a sampling site beside a heavily trafficked road in a city in southern Taiwan (Lin et al., 2006).

2.3 Seasonal variation of size distributions for elements

Since the sampling at the three sites was not carried out concurrently, in order to eliminate the influence of meteorological conditions on the size distribution of the elements, the EFs of elements are used for seasonal and spatial comparisons.

At Tsinghua urban site, the EFs of Al, Mg, Ca, Ti and Zr in winter are comparable with those in summer in coarse mode. It indicates that these elements are crust related in coarse mode in both seasons. The EFs of Be, S, Cr, Co, Ni, Cu, Ga, Se, Mo, Ag, Cd, Sb, Tl and Pb
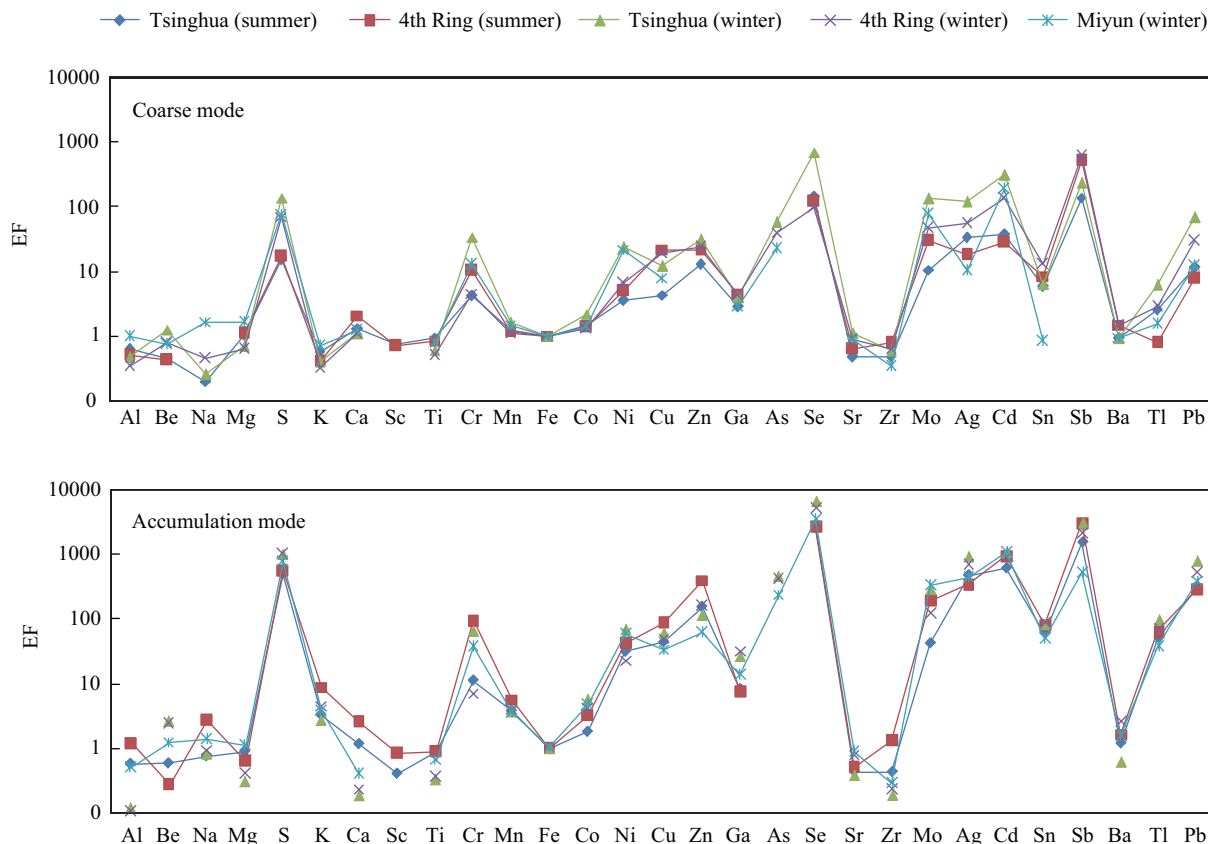
Fig. 3   Enrichment factors (EFs) of elements in coarse mode and accumulation mode particles in Beijing.

show higher values in winter than in summer in both accumulation and coarse modes. The elements of Be, Co, Ga show large accumulation mode in winter; however, much minor accumulation mode is found for them in summer. Therefore, these elements may mainly come from coal combustion for heating in winter, since high average abundance for them was found in Chinese coal (Zhao et al., 2002).

At 4th Ring curbside site, similar seasonal trend as that of at Tsinghua urban site is observed for crust related elements of Al, Mg, Ca, Ti and Zr and for possible coal combustion related elements of Be, S, Ga, Se, Ag, Cd, Tl and Pb. It indicates these elements may not be traffic related. However, Cr, Ni, Mo, Cu, Zn and Sb show no obvious seasonal variation at 4th Ring curbside site, while these metals have been reported emitted from diesel and gasoline engines (Wang et al., 2003; Lin et al., 2006), and similar size distribution for Cr and Ni has been observed beside a heavily trafficked road (Lin et al., 2006), which means that these elements are traffic related.

2.4 Spatial variation of size distributions for elements

The EFs are similar for crust related elements Al, Mg, Ca, Sc, Ti, Sr and Zr at the three sampling sites. However, at Miyun rural site, the EFs for coal burning and traffic related elements (Be, Zn, Cu, Ga, As, Se, Ag, Sn, Sb, Tl and Pb) are much lower than those at urban and curbside sites. It suggests serious element pollution at urban and curbside sites.

Since Cu/Sb is 110 in UCC (Taylor and McLennan, 1985), averagely 6.5 in Chinese coal (Zhao et al., 2002)

and about 4 in brake-lining (Weckwerth, 2001; Lin et al., 2006), Cu and Sb could be used as quantitative tracers associated with anthropogenic sources. In this study, Cu/Sb is 2.54–3.63 and 3.92–6.49 in accumulation and coarse mode respectively at urban and curbside sites. Cu and Sb in accumulation mode may be related to coal burning; however those in coarse mode may be related to brake-lining and coal burning fly ash. There is large coarse mode for Cu and Sb at curbside site; however, it is not obvious at urban site. The abundance of Cu and Sb in coarse mode at curbside site is about 2–6 times higher than that at urban site. It indicates traffic is a major coarse mode source for Cu and Sb at curbside.

The usage of leaded gasoline has been banned in Beijing since 1997. The concentration of Pb in 1999 decreased clearly compared with that in 1987 (Zhang et al., 2000). However, serious Pb pollution is still observed in Beijing (He et al., 2001; Sun et al., 2006). Industry emission, motor vehicle emission, coal burning, long-range transported dust from outside Beijing and the re-suspended soil containing the deposition of those from previously emitted leaded gasoline have been speculated as the important sources of Pb in Beijing (Sun et al., 2006). In this study, the concentration of Pb ranged from 32–468 ng/m^3. Comparable EFs of Pb in accumulation mode are found for samples collected at both Tsinghua urban site and 4th Ring curbside site, which suggests motor vehicle emission may be not a major source of Pb in Beijing since the leaded gasoline phased out. The lower EFs of Pb in coarse mode (8–67) than those in accumulation mode (276–764) indicate re-suspended soil is not a major source of Pb. However, the

EFs in accumulation mode in winter are about two times of that in summer, which indicates coal burning should be a major source of Pb, since coal consumption for heating will increase in winter. The EFs in both accumulation and coarse mode at rural site are lower than those of urban and curbside sites.

The EFs of Cr, Ni and Mo are 2.4–9.5 and 2.8–7.4 times higher at Tsinghua urban site than those at curbside site in winter. It suggests there may be local sources in the vicinity of Tsinghua urban site such as heating boilers.

3 Conclusions

A study on size distributions of elements was carried out at curbside, residential and rural sites in Beijing, China. High levels of Mn, Ni, As, Cd and Pb indicate the pollution of toxic heavy metals in Beijing cannot be neglected. PCA analysis indicates four sources, and of them combustion emission, crust related sources, traffic related sources and volatile species from coal combustion were identified. Grouped by size distribution and EFs, Al, Mg, Ca, Sc, Ti, Fe, Sr, Zr and Ba were found mostly concentrated in coarse mode, and they should be crustal related. S, As, Se, Ag, Cd, Tl and Pb were found mostly concentrated in accumulation mode, and they should be mainly fossil fuel related. Be, Na, K, Cr, Mn, Co, Ni, Cu, Zn, Ga, Mo, Sn and Sb were found multi-modal. Crust soil, re-suspended soil, vehicle emission and coal combustion may contribute to their levels in the atmosphere. The EFs of Be, S, Cr, Co, Ni, Cu, Ga, Se, Mo, Ag, Cd, Sb, Tl and Pb show higher values in winter than in summer in both accumulation and coarse modes at Tsinghua urban site. These elements may mainly come from coal combustion for heating in winter, since high average abundance for them was found in Chinese coal. However, Cr, Ni, Mo, Cu, Zn and Sb did not show obvious seasonal variation at 4th Ring curbside site. These elements may be traffic related. At Miyun rural site, the EFs for coal burning and traffic related elements (Be, Zn, Cu, Ga, As, Se, Ag, Sn, Sb, Tl and Pb) are much lower than those at urban and curbside sites. It suggests serious pollution at urban and curbside sites. The abundance of Cu and Sb in coarse mode at curbside site is about 2–6 times higher than that at urban site. It indicates traffic is a major coarse mode source for Cu and Sb at curbside. Instead of vehicle emission, coal burning can be a major source of Pb in Beijing since the phase out of leaded gasoline as the EFs of Pb are comparable in accumulation mode at urban site and curbside site and about two times higher in winter than that in summer.

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