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Characteristics and sources of lead pollution after phasing out leaded gasoline in Beijing

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Abstract

A 5-year long-term programme of Pb-monitoring from 2000 to 2004 was carried out at three representative urban sites (a traffic, an industrial, and a residential site), and a suburban site to evaluate the pollution level of Pb in Beijing. For comparison, aerosol samples were also collected in four other cities, Shanghai, Qingdao, Duolun, and Yulin in China. Pb pollution in Beijing has been very serious when compared with other sites over the world, as the concentration of Pb in Beijing remained as high as ~100–300 ng m^{-3} in fine particles ($PM_{2.5}$). Significant spatial variation of Pb in summer with the highest concentration at the industrial site was observed, while relatively even spatial variation was found in winter in urban area, although much heavier in the urban area than at suburban site. Strong seasonal variation of ~2–3 times higher Pb concentration in winter than that in summer was found. Pb exhibited a unimodal size distribution with most of it in fine fraction. Pb in fine particles was enriched by a factor of 200–1600 relative to its abundance in crust. Besides industry emission, motor vehicle emission, and coal burning, long-range transported dust from outside Beijing and the re-suspended soil containing the deposition of those from previously emitted leaded gasoline could be the important sources of Pb in Beijing.

Keywords: Lead; Urban pollution; Atmospheric pollution; Sources; China; Beijing

1. Introduction

Lead, the only metal listed in the National Ambient Air Quality Standard of China, has attracted public attention for several decades because of its adverse effects on human health, especially on children's growth and intelligence. It was reported (Chen et al., 2003) that the blood lead level of 35.7% children at Beijing in 2001 exceeded the Pb poisoning standard (100 μg L^{-1}) regulated by

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the World Health Organization (Centers for Disease Control and Prevention, 1991). Pb in the atmosphere can be deposited in urban soils (Wong and Li, 2004), and may then be re-suspended to re-enter the atmosphere (Young et al., 2002). This could increase human exposure to Pb and cause long-term potential health effects (Nriagu and Pacyna, 1988). Thus, monitoring Pb pollution has been one of the major tasks in controlling air pollution worldwide.

The global emission of trace elements increased significantly due to anthropogenic activities before 1970s (Nriagu, 1979). Among these trace elements, the increase of Pb is largely attributed to the vehicles and roadside emissions (Nriagu, 1989). Pb contributes more than 20% of the total mass of those fine particles emitted from burning of leaded gasoline, of which approximately 75% is emitted directly to the atmosphere (Pacyna, 1998). Tetraethyl Pb was first introduced as anti-knocking gasoline additives in the 1920s, and Pb concentration in the atmosphere continually increased from that time, although it has declined in the last few decades. Until 1970s, when the toxicity of Pb was realized, the airborne Pb concentrations in USA, Japan, and many countries in Europe first began to decrease due to the phase-out of leaded gasoline. In California Pb concentration declined from $\sim$3000 ng m^{-3} in the early 1970s (Miller et al., 1972) to less than 10 ng m^{-3} (Chow et al., 1996) in 1990s. In China, the use of leaded gasoline was banned first in Beijing in 1997, and then in Shanghai, Guangzhou, Tianjin and other big cities. Wang et al. (2003) evaluated the phase-out of leaded gasoline in Tianjin using isotope techniques (^{206}Pb/^{207}Pb). They found that Pb concentration in 1994–2001 decreased a little, while Pb isotope ratio (^{206}Pb/^{207}Pb) increased gradually. The results indicated that the contributions from vehicles emission decreased, whereas those from other sources likely increased. The results based on the individual particle analysis with the pattern recognition technique combined with micro-PIXE spectrum indicated that the low level Pb concentration in most unleaded gasoline particles was still the important input of Pb to the atmosphere in Shanghai. The other four major sources of lead were cement industry, coal combustion, oil combustion, and metallurgic industry (Wang et al., 2000). However, studies on Pb pollution at Beijing are rather limited. Pb concentration in 1999 decreased clearly compared with that in 1987 (Zhang et al., 2000). He et al. (2001) reported the annual Pb average concentration of 0.30 μg m^{-3} in 1999–2000 in Beijing and those possible sources, such as re-entrained dust, transport from areas outside Beijing, vehicles using leaded fuel coming from other places into Beijing, non-automobile sources, were speculated. Beijing remains high concentration of Pb after the phase-out of leaded gasoline and, however, the sources of Pb are poorly understood. The question of the heavy Pb pollution and its sources must be addressed urgently. In this study, we report a long-term monitoring of Pb from 2000 to 2004 in Beijing and try to answer the question mentioned above.

2. Experimental

2.1. Sampling

Aerosol samples of total suspended particles (TSP), with aerodynamic diameters of less than 100 μm, PM_{10} (particles with aerodynamic diameters of less than 10 μm), and $PM_{2.5}$ (particles with aerodynamic diameters of less than 2.5 μm) were collected in different seasons from 2000 to 2004 at five cities of China (see Fig. 1), i.e. Beijing, Shanghai, Qingdao, Yulin, and Duolun. The detailed descriptions of sampling sites are summarized in Table 1.

TSP, PM_{10}, and $PM_{2.5}$ aerosol samples were all collected on Whatman® 41 filters (Whatman Inc.,

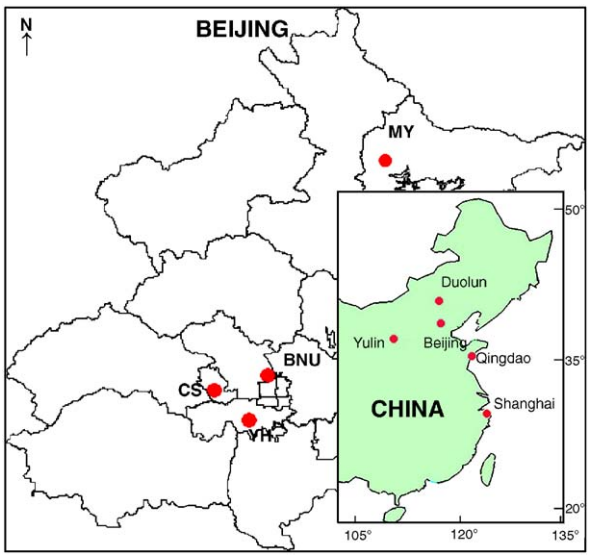

Fig. 1. Geographical locations of sampling sites in this study (BNU: Beijing Normal University; CS: Capital Steel Company; YH: Yihai Garden; MY: Miyun Hydrologic Station).

Table 1
A summary of sampling information and relevant environmental parameters in five cities of China

City	Environment	Description	Year	Season	Annual P[a]	Mean T[b]	Population[c]
Beijing					338.9	12.9	1128
BNU	Traffic	Twelve-story building of science and technology (~40 m) in Beijing Normal University between the 2nd and 3rd ring roads	2001	Winter			
			2002	Spring			
			2002	Summer			
			2002	Winter			
			2003	Spring			
			2003	Autumn			
			2004	Spring			
CS	Industrial	A building (~4 m) close to Capital Steel Company	2002	Summer			
			2002	Winter			
YH	Residential	A residential building (~40 m) in Yihai Garden near the South 4th Ring Road	2002	Summer			
			2002	Winter			
MY	Suburban	A building (~4 m) in Miyun Hydrologic Station	2003	Spring			
			2003	Autumn			
			2004	Spring			
Shanghai	Suburban	Five-story teaching building (~15 m) in Fudan University	2003	Autumn	1200	16.0	1674
			2004	Spring			
Qingdao	Coastal	Three-story meteorological station (~10 m) on the top of Baguan hill in the Ocean University of China	2004	Spring	776	12.2	707
Yulin	Suburban	Four-story building (~10 m) in Shaanxi Research Institute for Sand Control	2004	Spring	414	8.1	41
Duolun	Urban	Four-story Teaching Building (~10 m) in the No. 3 Middle School	2003	Spring	385	1.6	10
			2003	Autumn			
			2004	Spring			

[a] P = Precipitation (mm).
[b] T = Temperature (°C).
[c] Units in 10,000.

Maidstone, UK) using medium-volume samplers manufactured by Beijing Geological Instrument-Dickel Co., Ltd. (model: TSP/PM_{10}/$PM_{2.5}$−2; flow rate: 77.59 L min^{-1}). All those filters were weighed before and after sampling with an analytical balance (Sartorius 2004MP, reading precision 10 μg) after stabilizing in constant temperature (20 ± 5°C) and humidity (40 ± 2%). All the procedures were strictly quality-controlled to avoid any possible contamination of the samples. To study further the sources of Pb, soil samples were also collected at seven typical sites located in different geographical areas with various sources at Beijing: downtown areas of second ring road, of third ring road, of fourth ring road, a place near a gas station, a residential area, an industry area, and a construction area. For comparison, the soil samples were also collected at Duolun in Inner Mongolia, one of the sources of dust storm. The detailed information on soil sampling was given in Han et al. (2005).

Sixteen sets of size-segregated samples were collected on the top of a two-floor building (~6 m high) from August 2000 to March 2001 at the Institute of Atmospheric Physics, Chinese Academy of Science in Beijing using Battelle-type cascade impactors (the flow rates is approximately 1.25 L m^{-3}), which has eight size-fractionated stages with the size range of <0.25, 0.25–0.5, 0.5–1, 1–2, 2–4, 4–8, 8–16 and >16 μm respectively. The 50% cut off diameters (D_{50}) of eight impactor stages were 0.12, 0.25, 0.50, 1.0, 2.0, 4.0, 8.0, 16 μm respectively. The sampling usually started at 8:00 a.m. and ended at 6:00 p.m., and then another sample was collected from 6:00 p.m. to 8:00 a.m. the next day.

2.2. Chemical analysis

The sample filters were digested at 170 °C for 4 h in high-pressure Teflon digestion vessel with 3 mL concentrated HNO_3, 1 mL concentrated HCl, and 1 mL concentrated HF. After cooling, the solutions were dried, and then diluted to 10 mL with distilled–deionized water. In total, 23 elements including Pb were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Model: ULTIMA, JOBIN-YVON Company, France). The detailed analytical procedures are given elsewhere (Zhuang et al., 2001, 2003). The soil samples were first sieved, only allowing particles with diameter smaller than 30 μm to pass through, and then they were analyzed following the methods above.

3. Results and discussion

3.1. Pb level in Beijing

The concentrations of Pb at four sites in Beijing from 2001 to 2004 and at other cities in China from 2003 to 2004 are presented in Table 2. The quarterly and annual average of National Ambient Air Quality Standard for Pb is not to exceed 1.5 and

Table 2
Statistical summary of Pb concentrations (ng m^{-3}) in five cities of China

City	Sampling period	TSP				PM_{10}				$PM_{2.5}$			
		Mean	SD	Range	*N*	Mean	SD	Range	*N*	Mean	SD	Range	*N*
Beijing													
BNU	Win-01	235.8	231.1	9.8–813.1	35	187.9	147.4	15.9–600.5	32	206.0	193.9	33.3–760.1	19
	Spr-02	236.9	176.5	8.4–850.8	81	104.1	103.5	3.3–495.7	31	124.7	124.6	0.0–558.4	43
	Sum-02	93.6	27.6	69.9–123.8	3	112.5	86.6	5.2–268.0	18	109.6	53.9	36.5–206.8	19
	Win-02					365.2	365.9	68.7–1534.3	19	310.9	328.0	44.6–1446.5	20
	Spr-03	303.4	322.2	17.6–1348.9	28	233.5	206.2	12.0–907.0	28	135.8	115.0	11.3–421.3	20
	Aut-03	193.9	164.3	14.4–639.8	20					186.2	202.6	8.9–943.1	22
	Spr-04	307.0	262.0	9.3–990.8	41					175.7	145.3	8.2–595.9	50
CS	Sum-02					218.8	106.1	46.2–483.2	22	198.2	95.5	51.0–467.1	21
	Win-02					463.9	395.2	36.0–1524.0	18	265.1	174.8	19.0–702.8	20
YH	Sum-02					112.5	78.7	4.1–286.0	21	101.9	48.0	15.5–196.5	20
	Win-02					490.6	422.9	65.8–1735.9	18	316.3	233.1	57.6–881.7	20
MY	Spr-03					129.8	130.1	3.1–501.2	31	70.2	58.8	0.0–199.3	26
	Aut-03	139.7	135.1	0.4–442.6	18					98.7	89.1	2.1–298.2	20
	Spr-04	147.3	162.0	3.6–656.8	47					195.0	186.2	7.1–629.4	47
Shanghai	Aut-03	45.5	40.9	7.0–169.4	19					39.3	31.4	1.8–141.5	19
	Spr-04	176.1	145.5	38–546	22					85.5	64.0	18.0–290.5	32
Qingdao	Spr-04	156.3	144.8	13.4–650	37					161.4	139.0	4.8–696.2	43
Yulin	Spr-04	69.6	63.3	4.6–295.1	44					43.4	44.1	2.5–226.3	46
Duolun	Spr-03	43.3	28.0	7.5–117.7	30								
	Aut-03	27.9	23.8	1.4–90.3	13					34.5	33.8	3.6–107.4	13
	Spr-04	30.1	41.8	2.1–222.5	33					28.6	32.2	4.8–149.6	46

Note: Spr = Spring, Sum = Summer, Aut = Autumn, and Win = Winter.

1.0 μg m^{-3}, respectively. Although the average concentrations of Pb at the urban site (BNU, CS, and YH), and suburban site (MY) reported in this study were below the standard, it could be seen clearly that a considerable amount of Pb was found in the atmosphere of Beijing. The highest average concentration of Pb in the urban area in TSP, PM_{10}, and $PM_{2.5}$ in different season was 307.0, 490.6, and 316.3 ng m^{-3}, respectively. Even if the lowest seasonal average concentration, it was high up to 93.6, 104.1, and 101.9 ng m^{-3} in TSP, PM_{10} and $PM_{2.5}$, respectively. The highest average concentration of Pb at suburban site was 195.0 ng m^{-3} in $PM_{2.5}$ in spring of 2004 and the lowest was 70.2 ng m^{-3} in spring of 2003. The results indicated that, though leaded gasoline has been banned in Beijing since 1997, Pb pollution is still very serious in Beijing, and it is much heavier in urban area than suburban area. As the number of motor vehicles in Beijing increased by 10–15% per year in the recent years and reached 2.2 million in the first half year of 2004, the motorization of the city has brought much more air pollutants, including Pb, to the atmosphere. The atmospheric Pb concentrations in Beijing and other cities of China reported previously are shown in Table 3. The pollution level of Pb in Beijing in the early 1980s was ~90 ng m^{-3} (Winchester and Bi, 1984). As the rapid increase of motor vehicles, Pb concentration reached ~200 ng m^{-3} in the late 1980s (Chen et al., 1994) and remained in a high level in the following few years. Hu and Wu (1999) investigated the Pb pollution level in four cities of China, i.e., Guangzhou, Wuhan, Lanzhou, and Chongqing, from 1995 to 1996, and found that the concentration of Pb in $PM_{2.5}$ was as high as to 476.4 ng m^{-3} in Guangzhou and even to 635.9 ng m^{-3} in Lanzhou. Beijing first prohibited the use of leaded gasoline in July 1997. However, Pb concentration in the atmosphere has not decreased markedly since then. The annual average Pb concentration in $PM_{2.5}$ at a residential site (Tsinghua University) and a downtown site (Chegongzhuang) in Beijing from 1999 to 2000 was 335 and 304 ng m^{-3}, respectively (He et al., 2001), while it was 280 and 270 ng m^{-3} at a downtown site (Hainan Road) and a residential site (Tongji University), respectively, in Shanghai (Ye et al., 2003). Our 5-year long-term programme of Pb-monitoring from 2001 to 2004 showed that Pb in $PM_{2.5}$ in Beijing maintained levels of ~100–300 ng m^{-3}. The highest average concentration of Pb was 316.3 ng m^{-3} at the residential site (YH) in winter of 2002 and the lowest average concentration was 70.2 ng m^{-3} at the suburban site (MY) in spring of 2003. The results above indicated that Pb pollution remained a high level in the past few years even after phasing out of leaded gasoline in Beijing.

3.2. Comparison with other sites in the world

The concentrations of Pb in ambient suspended particulates at different cities around the world are listed in Table 3. When compared with those reported previously at other sites in Asia, America, and Europe, it was found clearly that the pollution level of Pb in Beijing was the heaviest among all of these cities reported. Similar studies carried out in other urban areas of Asia reported concentrations of only 76.86 and 91.62 ng m^{-3} at a traffic site (Hung Hom) and an industrial site (Kwun Tong), respectively, in Hong Kong (Ho et al., 2003), and 200 ng m^{-3} at Seoul in Korea (Mishra et al., 2004). The low Pb concentration of 34 ng m^{-3} in $PM_{2.5}$, 36 ng m^{-3} in PM_{10}, and 44 ng m^{-3} in TSP in the winter of 2000 were found at a traffic site in Taichung in Taiwan (Fang et al., 2002). Pb concentrations reported in most of the sites in Europe and America were distinctly lower than those in Beijing. Gao et al. (2002) reported the Pb concentration of only 4.9–7.9 ng m^{-3} in $PM_{2.5}$ at three locations over New Jersey near New York from 1998 to 2000. The low Pb concentration of ~6 ng m^{-3} in fine particles was observed in Helsinki in Finland from 1996 to 1997 (Pakkanen et al., 2001). Similar level of Pb ranging from 1–11 ng m^{-3} was also observed at ten sites in the central California in the early 1990s (Chow et al., 1996). It is clear from these comparisons that the atmosphere in Beijing is still heavily Pb polluted.

3.3. Spatial variation of Pb in Beijing

To better evaluate the pollution level of Pb in Beijing, Pb concentrations at four sites of Beijing (BNU, CS, YH, and MY) were compared with other four cities in China. Pb showed significant spatial variations in summer in Beijing (one-way ANOVA, $p<0.001$ at a significance level of 95%). The average concentration of Pb in summer of 2002 was 218.8 and 198.2 ng m^{-3} in PM_{10} and $PM_{2.5}$, respectively, at the industrial site, CS, nearly double that at the other two sites, BNU and YH. The concentrations of chemical species at a specific location are strongly determined by the distances

Table 3
The atmospheric Pb concentrations (ng m^{-3}) in Beijing and other cities over the world

Site	Period	Mean	Type	Instrument	Environment	Source
1. Asia (China)						
Beijing						
	July 1980	310	$PM_{2.0}$	PIXE	Urban	Winchester and Bi (1984)
		72	$PM_{>2.0}$			
	December 1980	90	$PM_{2.0}$			
		92	$PM_{>2.0}$			
Tiananmen	30 April 1989–14 May 1990	210	$PM_{2.5}$	XRF	Traffic	Chen et al. (1994)
Chenggongzhuang	July 1999–September 2000	304	$PM_{2.5}$	XRF	Urban	He et al. (2001)
Tsinghua		335	$PM_{2.5}$		Subarban	
Guangzhou	1995–1996	476.4	$PM_{2.5}$	XRF	Traffic	Hu and Wu (1999)
Wuhan		310.4	$PM_{2.5}$		Urban	
Lanzhou		635.9	$PM_{2.5}$		Urban	
Chongqing		220.4	$PM_{2.5}$		Urban	
Shanghai						
Hainan Road	March 1999–March 2000	280	$PM_{2.5}$	XRF	Urban	Ye et al. (2003)
Tongji		270	$PM_{2.5}$	XRF	Suburban	
2. Asia (Taiwan)						
Taichung						
CCRT	2 November–30 November 2000	34	$PM_{2.5}$	AAS	Traffic	Fang et al. (2002)
		36	PM_{10}			
		44	TSP			
3. Asia (Hong Kong)						
Hung Hom	November 2000–February 2001	76.86	$PM_{2.5}$	ICP-MS	High traffic	Ho et al. (2002)
		98.74	PM_{10}			
Kwon Tong	November 2000–February 2001	91.62	$PM_{2.5}$		Industrial	
		100.5	PM_{10}			
4. Asia (Korea)						
Seoul	March–May 2001	120	PM_{10}	ICP-AES	Urban	Kim et al. (2003)
	9–25 December 2002	200	PM_{10}	ICP-AES	Urban	Mishra et al. (2004)
Jeju	9–25 December 2002	27.6	PM_{10}	ICP-AES	Rural	Mishra et al. (2004)
5. North America (USA)						
New York						
Sandy Hook	January 1998–July 1999	4.9	$PM_{2.5}$	ICP-MS	Coastal	Gao et al. (2002)
Liberty Science Center	October 1998–January 2000	7.9	$PM_{2.5}$		Urban	
New Brunswick	January 1998–December 1999	6.6	$PM_{2.5}$		Urban	
Central California	13 July–24 August 1999	1–11	$PM_{2.5}$	XRF	Total	Chow et al. (1996)
6. Europe (Finland)						
Helsinki	October 1996–May 1997	5.8	$PM_{2.3}$	PIXE	Urban	Pakkanen et al. (2001)
		5.5	$PM_{2.3}$		Rural	
		2.0	$PM_{2.3–15}$		Urban	
		0.63	$PM_{2.3–15}$		Rural	

from the sources, which could reflect the emissions from those point sources. CS site is located at a place close to Capital Steel Plant, the largest emission source of those industrial pollutants. Thus the highest concentration of Pb at the industrial site, CS, indicated that the industry emission could be an important source of Pb in Beijing. The spatial variation of Pb in winter in both PM_{10} and $PM_{2.5}$ was relatively even (one-way ANOVA, $p > 0.5$ at a significance level of 95%). The average concentrations of Pb were 365.2, 463.9, and 490.6 ng m^{-3} in PM_{10}, and 310.9, 265.1, and 316.3 ng m^{-3} in $PM_{2.5}$ at BNU, CS, and YH, respectively, in the winter of 2002. The higher concentration of Pb at YH site could be ascribed to the coal combustion in heating season plus the industrial pollutants from the

up-wind area of CS brought by the northwest wind. The average concentrations of Pb at the suburban site, MY, were 139.7 ng m^{-3} in TSP and 98.7 ng m^{-3} in $PM_{2.5}$, respectively, both much lower than that at the traffic site, BNU, in autumn of 2003. In the spring of 2004, the Pb concentration in TSP was similar to that in autumn of 2003, while in $PM_{2.5}$, MY even showed higher Pb concentration than that at BNU site. Dust storm in spring carries significant quantities of pollutants, which are from the mixing of mineral aerosol with pollution aerosol such as industrial soot, toxic metals and acidic gases on the transport pathway (Sun et al., 2004b). The high concentration of Pb in spring at suburban site indicated that large part of Pb in fine particles was likely from the long-range transported dust from outside Beijing.

The pollution level of Pb in Beijing was the heaviest among the five cities of China, i.e. Beijing, Shanghai, Qingdao, Duolun, and Yulin. The average concentrations of Pb in autumn of 2003 in Shanghai were 45.5 and 39.3 ng m^{-3} in TSP and $PM_{2.5}$, respectively, nearly five times lower than those in Beijing. In the spring of 2004, TSP and $PM_{2.5}$ samples were collected synchronously at the five cities, the concentration of Pb in Beijing was nearly twice higher than that in Shanghai. Although the usage of the leaded gasoline had been officially prohibited for 2 years in Shanghai, the automobile exhaust still contributed most of Pb pollution to the atmosphere in Shanghai (Wang et al., 2000). The number of motor vehicles rapidly increased and reached near to 1.7 million in 2004 in Shanghai, close to that in Beijing (2.2 million), which could have much heavier Pb pollution in Shanghai than other small cities. Even so, Pb concentration in Beijing was still higher than that in Shanghai. The pollution level of Pb in TSP in Qingdao was comparable with that in Shanghai (two sample t-test, $p = 0.614$ at the 0.05 level), while the concentration of 161.4 ng m^{-3} of Pb in $PM_{2.5}$ in Qingdao was close to that in Beijing (175.7 ng m^{-3}), but nearly twice higher than that in Shanghai (85.5 ng m^{-3}). Qingdao is a coastal city which, at the end of 2003, possessed over a million motor vehicles. In spring, dust storm mixing pollutants on the pathway passes through Qingdao, making the air pollution worse than other seasons. Thus the high concentration of Pb in Qingdao was likely from the local emissions plus the vehicle emissions in Northern China brought into Qingdao by dust storm (Guo et al., 2004). The concentration of Pb in Duolun was ~30 ng m^{-3} in both TSP and $PM_{2.5}$. The concentration of Pb in Yulin was also less than 100 ng m^{-3}. Duolun is located near the Hunshandake sand desert and Yulin near the Mu Us desert. Both the two sites showed much lower concentration of Pb compared with Beijing, as they have much fewer vehicles plus the clean air brought by westerly winds with cold fronts frequently passed through them.

3.4. Temporal and seasonal variations of Pb in Beijing

Fig. 2 shows the variations of Pb in TSP, PM_{10}, and $PM_{2.5}$ at BNU site from 2001 to 2004. Although the average concentrations of Pb in TSP, PM_{10}, and $PM_{2.5}$ were all below the National Ambient Air Quality Standard, a few peaks that exceeded the National standard, mostly concentrated in winter/spring, were observed. For example, the highest concentrations of Pb reached 1446.5, 1534.3, and 1348.9 ng m^{-3} in $PM_{2.5}$, PM_{10}, and TSP, respectively, all higher than the annual average standard of 1000 ng m^{-3}. The concentration of Pb showed significant daily variations in winter ranging from 9.8 to 813.1 ng m^{-3} in TSP in winter of 2001, and 68.7–1534.3 ng m^{-3} in PM_{10} and 44.6–1446.5 ng m^{-3} in $PM_{2.5}$ in the winter of 2002. Relatively minor temporal variation of Pb was observed in summer. As the temporal variations are largely determined by the strength of source emission, the significant variations of Pb in winter were likely due to more pollution sources in winter than other seasons. In addition, the meteorological conditions, such as temperature, relatively humidity, and wind speed, positively or adversely affect the dispersion of Pb.

Seasonal variation of Pb is also exhibited in Fig. 2. The concentration of Pb showed the highest value in winter, ~2–3 times higher than that in summer. At BNU site, the concentration of Pb in $PM_{2.5}$ was 206.0 and 310.9 ng m^{-3} in winter of 2001 and 2002, respectively, ~2–3 times higher than 109.6 ng m^{-3} in the summer of 2002. The concentration of Pb in TSP reached 236.9, 303.4, and 307.9 ng m^{-3} in the spring of 2002, 2003, and 2004, all much higher than 93.6 ng m^{-3} in the summer of 2002 and 193.9 ng m^{-3} in the autumn of 2003. The higher concentrations of Pb in winter were likely from the much higher consumption of the domestic coal for heating and the vehicle exhausts in this season, as more coal is burned for the domestic heating in winter and the emission from the automobiles would produce

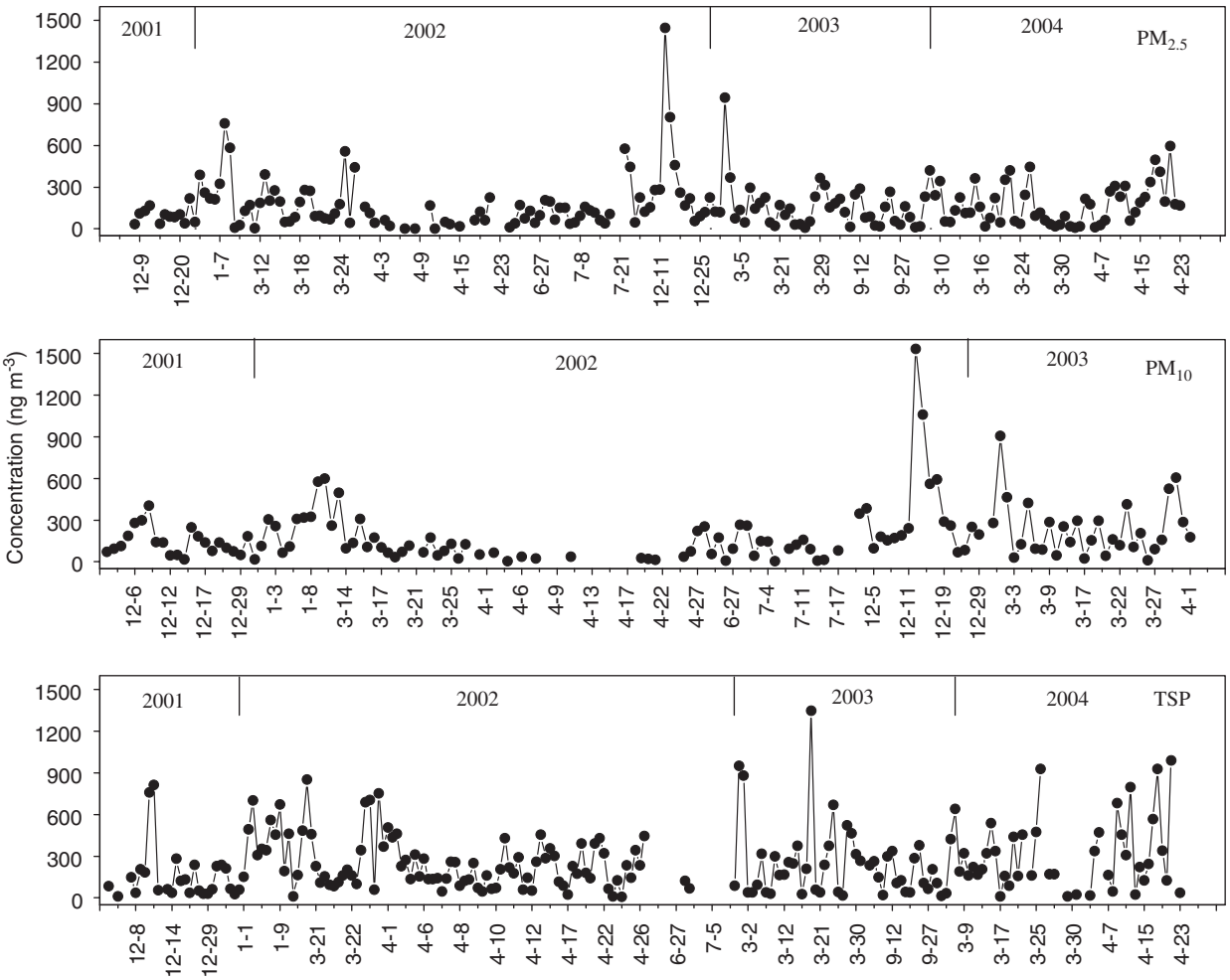

Fig. 2. Variations of Pb in TSP, PM_{10}, and $PM_{2.5}$ at BNU site from 2001 to 2004.

higher exhausts in the cold season due to the incomplete combustion of fuel running in colder weather (Simpson and Xu, 1994). The high concentrations of Pb in spring were likely due to coal combustion for heating in winter, plus the pollutants brought by dust storms, which affect Beijing frequently in spring. Meteorological conditions could also be the factors affecting the level of Pb. The low wind speed and low temperature in winter favor accumulation of pollutants, while the high temperature in summer favors the air convection and the dispersion of pollutants. In addition, more road dust, in which Pb deposited previously, could be re-suspended in winter due to the barer surface, while pollutants would be more easily washed out because of the ample precipitation in summer Though the high wind speed in spring favors the dispersion of pollutants, it could also re-suspend more pollution dust, which enhances the concentration of particles in the atmosphere. Moreover, the higher wind speed would introduce more transported dust, which mixes with large amounts of pollutants, including Pb, emitted on the pathway. Both these factors could increase the pollution level of Pb in Beijing.

3.5. Size distribution of Pb in Beijing

Knowledge of the size distribution is essential in understanding the sources of Pb and its effect on human health. Fig. 3 presents six sets of the size distribution of Pb from August 2000 to March 2001. The size distribution of Pb was mostly characterized by unimodal mode with the peak in the size range of 0.5–1 μm (29 September and 30 October, 2000). The unimodal size distribution of Pb with the peak in the

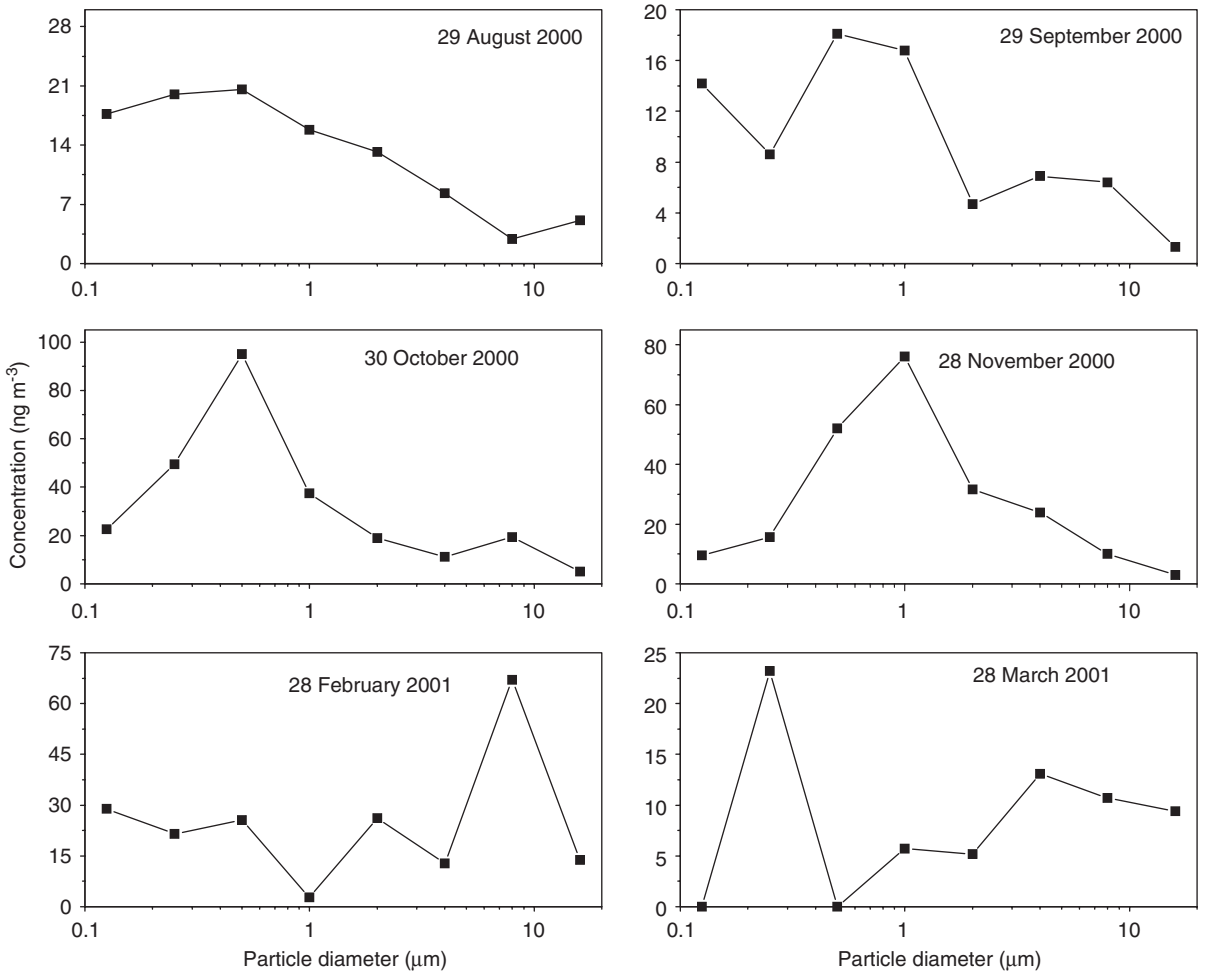

Fig. 3. Typical size distribution of Pb collected at the Institute of Atmospheric Physics, Chinese Academy of Science in Beijing from 2000 to 2001.

range of 4–8 μm was also observed on 28 February, 2001. However, bimodal model of Pb was sometimes found (28 March, 2001). The size distributions of Pb showed great changes in different seasons. For instance, the major part of Pb shifted from fine fractions in winter to coarse fractions in spring. Different size distributions suggest different sources. Pb in fine fraction with size smaller than 2 μm was usually from those anthropogenic sources, such as vehicle exhaust and coal combustion, while Pb in coarse fraction was from the natural sources, such as the re-suspension of road dust. Fig. 4 shows the variations of Pb concentration in fine particles (>2 μm) and coarse particles (>2 μm). The results indicated that most part of Pb in winter was

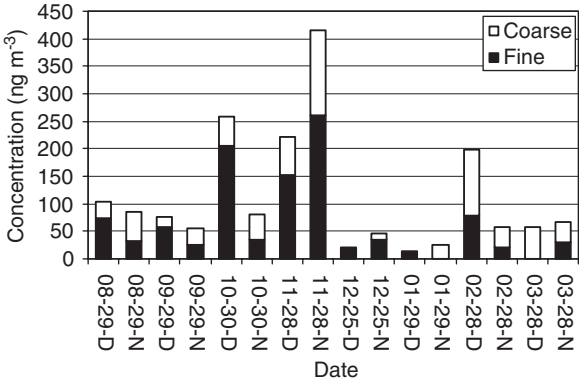

Fig. 4. Variations of Pb concentration in fine particles (>2 μm) and coarse particles (>2 μm) from 2000 to 2001 in Beijing (D: daytime; N: nighttime).

concentrated in fine fractions contributing more than ~60–80% of the total Pb. Pb in coarse particles contributed more of the total than that in fine particles in spring, which was likely due to more transported dust in this season. The transported dust mixed large amounts of pollutants emitted from pollution sources on the pathway and then carried them to Beijing, which became one of the major sources of Pb in spring (Sun et al., 2005). The comparison of Pb concentrations between day and night is also shown in Fig. 4. Generally, the Pb concentration in fine particles in the daytime was higher than that at the nighttime, which would likely be due to more anthropogenic activities in the daytime, such as vehicle exhaust and industry emission, which could introduce more pollutants in fine particles than that at the nighttime.

3.6. Sources of Pb in Beijing

3.6.1. Enrichment factor (EF) of Pb

EF is usually used as the first step to evaluate the strength of pollution sources in relation with crustal sources (Gao et al., 1992). The EF for Pb is defined as

$$EF = (Pb/Al)_{sample}/(Pb/Al)_{crust},$$

where Al is selected as the reference element of crust. $(Pb/Al)_{aerosol}$ is the concentration ratio of Pb to Al in the aerosol sample, and $(Pb/Al)_{crust}$ is the average ratio of Pb to Al in crust (Taylor and McLennan, 1985). The EF of Pb was calculated and listed in Fig. 5. The results showed that the atmospheric concentration of Pb in $PM_{2.5}$ in Beijing was 200–1600 times higher than that in crustal soil. The high EF suggested that the dominant sources for Pb were non-crustal and a variety of pollutions emissions might contribute to its loading in the ambient air. Fig. 5 also illustrated the remarkably higher EF values of Pb in Beijing than other cities of China. For example, the element Pb in fine particles in Duolun and Yulin was enriched by a factor of only 27–46 relative to its natural abundance in crustal soil. These results suggest that Beijing is in heavy Pb pollution area compared with Duolun and Yulin, which are near the desert regions that are less influenced by the anthropogenic sources.

In Beijing, Pb pollution was heavier in urban areas than in suburban site. In addition, the industrial site, CS, and the residential site, YH, located downwind of CS, showed higher EF of Pb than that at traffic site BNU, which suggested that industry emission was an important source of Pb in Beijing as mentioned above. Coal combustion was another significant factor for the high concentration of Pb in Beijing, as the higher EF of Pb was generally found in winter, when more coal was used for heating than other seasons. We also noted much higher EF of Pb in $PM_{2.5}$ than those in PM_{10} and

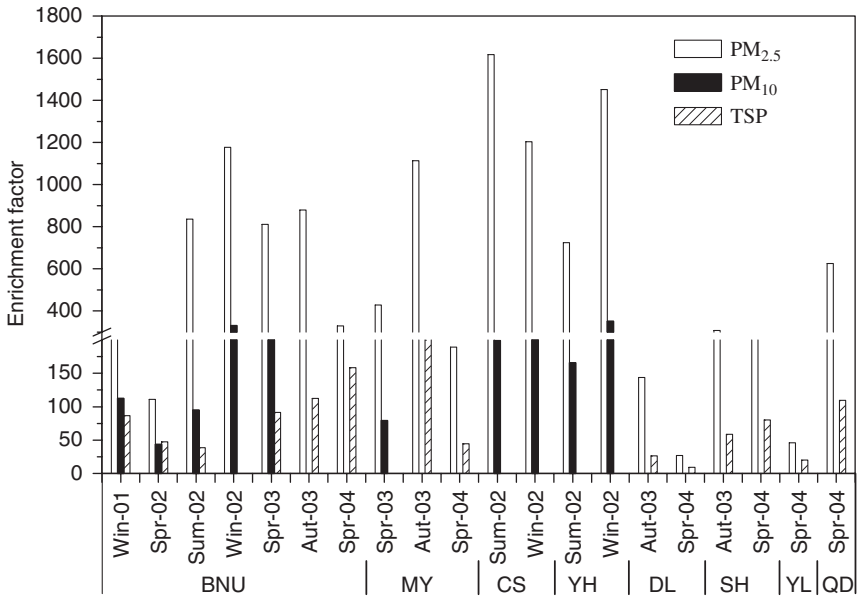

Fig. 5. Enrichment factor of Pb in different seasons from 2001 to 2004 at five cities of China (DL: Duolun; SH: Shanghai; YL: Yulin; QD: Qingdao).

TSP, which indicated that the pollution element, Pb, was more enriched in fine particles. Fine particles can enter the human body more easily than coarse particles and deposit in the tracheobronchial and alveolar regions of the lung, and Pb would be accumulated continuously and have more harmful effect on the human being.

Those soil particles contaminated could be re-suspended in the atmosphere by wind and become an important source of pollution elements (Young et al., 2002). In Beijing, Pb was enriched by 1.9–33.3 times in soil particles (<30 μm) compared with its natural crustal abundance, whereas the EF of Pb in those soil samples at Duolun in Inner Mongolia was close to unit (0.51–1.32), indicating that those soil in Duolun had hardly any Pb contamination. The high enrichment factor of Pb in Beijing soils was likely due to the input of the human activities, such as the deposition from previously emitted leaded-gasoline vehicle exhaust. Lankey et al. (1998) reported that over half of the total emitted lead is deposited on roads and those soils nearby. These particles would be re-suspended by vehicular movement/wind action and become one of major sources of Pb in the atmosphere.

3.6.2. Factor analysis

Factor analysis (FA, Varimax rotated principal component analysis) was performed with the elemental data sets of TSP, PM_{10}, and $PM_{2.5}$ respectively to further identify the possible sources of Pb in Beijing. To maximize the source-identification power, 12 species (the total mass, As, Zn, Pb, Ni, Cd, Fe, Mn, Ca, Cu, Al, and S) were selected. Five factors for TSP, and four factors for PM_{10} and $PM_{2.5}$, were resolved, as shown in Table 4. Five factors for TSP explained 93.4% of the total variance. The communities for all species were higher than 0.81, indicating the five factors identified were satisfactory. Among the five factors, the second factor was related to the source of Pb, which explained 20.0% of the variance. This factor showed high loadings for Zn, Pb, and S, representing the combined sources of industry emission, vehicle exhaust, and coal burning. The industrial metallurgical processes could produce the largest emissions of Zn, Cu, Ni, and Pb, while exhaust emissions from road vehicles also contain variable quantities of Zn, Cu, and Ni (Pacyna, 1998). As leaded gasoline has been banned since 1997 in Beijing, the emission of those vehicles should not be the dominant source of Pb in Beijing aerosols. However, the illegal use of

Table 4
Varimax rotated factor loading matrix for chemical species in TSP, PM_{10}, and $PM_{2.5}$[a]

	TSP						PM_{10}					$PM_{2.5}$				
	Factor1	Factor2	Factor3	Factor4	Factor5	Community	Factor1	Factor2	Factor3	Factor4	Community	Factor1	Factor2	Factor3	Factor4	Community
Mass	**0.97**	0.10	0.11	0.00	0.11	0.98	**0.89**	0.17	0.26	0.06	0.90	**0.57**	**0.57**	0.42	−0.06	0.83
As	0.24	0.18	0.04	0.01	**0.95**	0.99	0.09	0.41	0.10	**0.89**	0.98	0.41	0.00	0.26	**0.82**	0.91
Zn	0.00	**0.86**	0.34	0.15	0.06	0.88	0.03	**0.86**	0.16	−0.02	0.76	**0.84**	0.05	0.35	0.16	0.86
Pb	0.00	**0.84**	0.23	0.14	0.17	0.81	0.08	**0.88**	0.17	0.29	0.89	**0.85**	0.16	0.26	0.29	0.90
Ni	0.16	0.26	**0.92**	0.06	0.06	0.94	0.42	0.22	**0.85**	0.06	0.96	0.35	0.11	**0.88**	0.17	0.93
Cd	0.00	0.16	0.03	**0.98**	0.01	0.99	0.01	**0.85**	0.13	0.15	0.77	**0.76**	0.07	0.07	0.35	0.70
Fe	**0.98**	0.04	0.10	0.00	0.09	0.99	**0.98**	−0.03	0.12	0.02	0.97	0.05	**0.97**	0.01	−0.03	0.94
Mn	**0.98**	0.08	0.13	0.00	0.08	0.98	**0.95**	0.20	0.12	0.04	0.96	0.46	**0.80**	0.16	0.08	0.89
Ca	**0.93**	0.15	0.07	0.01	0.13	0.90	**0.92**	0.01	0.04	0.07	0.86	0.02	**0.91**	−0.03	0.12	0.85
Cu	0.16	0.25	**0.92**	−0.01	−0.01	0.94	0.08	0.26	**0.95**	0.07	0.98	0.30	0.10	**0.92**	0.13	0.97
Al	**0.98**	0.03	0.10	−0.01	0.04	0.98	**0.96**	−0.08	0.11	0.00	0.95	−0.11	**0.95**	0.17	−0.08	0.94
S	0.30	**0.85**	0.07	−0.03	0.02	0.81	0.08	**0.87**	0.12	0.15	0.81	**0.87**	−0.05	0.30	−0.01	0.85
% variance	40.8	20.0	16.0	8.4	8.2	93.4	38.7	28.0	15.3	7.8	89.8	30.8	30.7	18.4	8.1	88.1

[a]Factor loadings >0.70 are marked in bold.

leaded gasoline in the vicinal provinces and cities surrounding Beijing was found, which produced Pb pollution that could be transported into Beijing. Also, vehicles using leaded gasoline often travel from other cities to Beijing, which further worsens the burden of Pb in Beijing aerosols. Pb was found to be abundant in those dusts collected in the paved road, which was likely due to the deposition of those previously emitted exhausts of the leaded-gasoline vehicle. S exists mainly as sulphate, particularly, in the forms of ammonium sulphate, ammonium bisulphate, and sulphuric acid (Sweet and Gatz, 1998). The abundance of sulphate was strongly correlated with SO_2 in atmosphere that was mainly from the consumption of coal both in industry and in domestic families and, in turn, converted to sulphate through chemical transformation (Sun et al., 2004a). This factor with high loadings for Zn, Pb, and S indicated that vehicle exhaust, coal burning, and industry emission could be the multiple sources of Pb.

Four factors were retained when applying FA to PM_{10} and $PM_{2.5}$, which explained 89.8% and 88.1% of the variance, respectively. Among the four factors, the second factor in PM_{10} and the first factor in $PM_{2.5}$ were related to Pb, which were loaded with Pb, Zn, Cd, and S, indicating that industry emission, vehicle exhaust, and coal combustion were the combined sources of Pb pollution in the atmosphere in Beijing as discussed above for TSP.

4. Conclusions

A 5-year programme monitoring Pb was conducted at four sites in Beijing and the other four cities in China. Pb pollution in Beijing has been very serious when compared with other sites over the world, as the concentration of Pb in Beijing remained as high as $\sim$100–300 ng m^{-3} in fine particles ($PM_{2.5}$). Significant spatial variation of Pb in summer with the highest concentration at the industrial site was observed, while relatively even spatial variation was found in winter in urban area, although much heavier in the urban area than at suburban site. Strong seasonal variation of $\sim$2–3 times higher Pb concentration in winter than that in summer was found. Pb exhibited a unimodal size distribution with most of it in fine fraction. Pb in fine particles was enriched by a factor of 200–1600 relative to its abundance in crust. Major contributions to the atmospheric loading of Pb could include industry emission, motor vehicle emission, coal burning, and long-range transported dust from outside Beijing. Re-suspended soil that contained the deposition from previously emitted leaded-gasoline vehicle exhaust could be another important source of Pb. This work could provide the basic information in reducing the pollution level of Pb in Beijing.

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References

Centers for Disease Control and Prevention, 1991. Preventing lead poisoning in young children: a statement from the Centers for Disease Control and Prevention, Atlanta, 1991.

Chen, X., Teng, H., Wang, F., He, J., Zhou, S., Jian, Y., Xiao, X., 2003. Blood lead level and related risk factors among children aged 0–6 years in Beijing. Chinese Journal of Epidemiology 24 (10), 868–871 (in Chinese).

Chen, Z., Ge, S., Zhang, J., 1994. Measurement and analysis for atmospheric aerosol particulates in Beijing. Research of Environmental Sciences 7 (3), 1–9 (in Chinese).

Chow, J.C., Waston, J.G., Lu, Z., Lowenthal, D.H., Frazier, C.A., Solomon, P.A., Thuiller, R.H., 1996. Descriptive analysis of $PM_{2.5}$ and PM_{10} at regionally representative locations during SJVAQS/AUSPEX. Atmospheric Environment 30, 2079–2112.

Fang, G.C., Chang, C.N., Wu, Y.S., Fu, P.P.P., Yang, C.J., Chen, C.D., Chang, S.C., 2002. Ambient suspended particulate matters and related chemical species study in central Taiwan, Taichung during 1998–2001. Atmospheric Environment 36, 1921–1928.

Gao, Y., Arimoto, R., Duce, R.A., Lee, D.S., Zhou, M.Y., 1992. Input of atmospheric trace elements and mineral matter to the Yellow Sea during the spring of a low-dust year. Journal of Geophysical Research 97 (D4), 3767–3777.

Gao, Y., Nelson, E.D., Field, M.P., Ding, Q., Li, H., Sherrell, R.M., Gigliotti, C.L., Van Ry, D.A., Glenn, T.R., Eisenreich, S.J., 2002. Characterization of atmospheric trace elements on $PM_{2.5}$ particulate matter over the New York–New Jersey harbor estuary. Atmospheric Environment 36, 1077–1086.

Guo, Z., Feng, J., Fang, M., Chen, H., Lau, K.H., 2004. The elemental and organic characteristics of $PM_{2.5}$ in Asian dust

episodes in Qingdao, China, 2002. Atmospheric Environment 38, 909–919.

Han, L., Zhuang, G., Sun, Y., Wang, Z., 2005. Local and non-local sources of airborne particulate pollution at Beijing—the ratio of Mg/Al as an element tracer for estimating the contributions of mineral aerosols from outside Beijing. Science in China (Ser. B) 48 (4), 253–264.

He, K., Yang, F., Ma, Y., Zhang, Q., Yao, X., Chan, C.K., Cadle, S., Chan, T., Mulawa, P., 2001. The characteristics of $PM_{2.5}$ in Beijing, China. Atmospheric Environment 35, 4959–4970.

Ho, K.F., Lee, S.C., Chan, C.K., Yu, J.C., Chow, J.C., Yao, X., 2003. Characterization of chemical species in $PM_{2.5}$ and PM_{10} aerosols in Hong Kong. Atmospheric Environment 37, 31–39.

Hu, W., Wu, G.P., 1999. The lead pollution level in particulate of the four cities in China. Environmental Monitoring in China 15 (3), 5–7.

Kim, K.H., Choi, G.H., Kang, C.H., Lee, J.H., Kim, J.Y., Youn, Y.H., Lee, S.R., 2003. The chemical composition of fine and coarse particles in relation with the Asian dust events. Atmospheric Environment 37, 753–765.

Lankey, R.L., Davidson, C.I., McMichael, F.C., 1998. Mass balance for lead in the California south coast in air basin: an update. Environmental Research Section A 78, 86–93.

Miller, M.S., Friedlander, S.K., Hidy, G.M., 1972. A chemical element balance for the Pasadena aerosol. Journal of Colloid and Interface Science 39, 165–176.

Mishra, V.K., Kim, K.H., Kang, C.H., Choi, K.C., 2004. Winter time and distribution of airborne lead in Korea. Atmospheric Environment 38, 2653–2664.

Nriagu, J.O., 1979. Global inventory of natural and anthropogenic emissions of trace metals to the atmosphere. Nature 279, 409–411.

Nriagu, J.O., 1989. A global assessment of natural sources of atmospheric trace metals. Nature 338, 47–49.

Nriagu, J.O., Pacyna, J.M., 1988. Quantitative assessment of worldwide contamination of air, water and soils by trace metals. Nature 333, 134–139.

Pacyna, J.M., 1998. Source inventories for atmospheric trace metals. In: Harrison, R.M., Van Grieken, R. (Eds.), Atmospheric Particles, IUPAC Series on Analytical and Physical Chemistry of Environmental Systems, Vol. 5. Wiley, Chichester, UK, pp. 385–423.

Pakkanen, T.A., Loukkola, K., Korhonen, C.H., Aurela, M., Makela, T., Hillamo, R.E., Aarnio, P., Koskentalo, T., Kousa, A., Maenhaut, W., 2001. Sources and chemical compositions of atmospheric fine and coarse particles in the Helsinki area. Atmospheric Environment 35, 5381–5391.

Simpson, R.W., Xu, H., 1994. Atmospheric lead pollution in an urban area-Brisbane, Australia. Atmospheric Environment 28, 3073–3082.

Sun, Y., Zhuang, G., Wang, Y., Han, L., Dan, M., Guo, J., Zhang, W., Wang, Z., Hao, Z., 2004a. The air-borne particulate pollution in Beijing-concentration, composition, distribution and sources. Atmospheric Environment 38, 5991–6004.

Sun, Y., Zhuang, G., Yuan, H., Zhang, X., Guo, J., 2004b. Characteristics and sources of 2002 super dust storm in Beijing. Chinese Science Bulletin 49 (7), 698–705.

Sun, Y., Zhuang, G., Wang, Y., Zhao, X., Li, J., Wang, Z., An, Z., 2005. Chemical composition of dust storm in Beijing and implications for the mixing of mineral aerosol with pollution aerosol on the pathway. Journal of Geophysical Research—Atmosphere, 110, D24209, doi:10.1029/2005JD006054.

Sweet, C.W., Gatz, D.F., 1998. Summary and analysis of available PM2.5 measurements in Illinois. Atmospheric Environment 32, 1129–1133.

Taylor, S.R., McLennan, S.M., 1985. The Continental Crust: Its Composition and Evolution. Blackwell, Oxford, England.

Wang, J., Guo, P., Li, X., Zhu, J., Reinert, T., Heitmann, J., Spemann, D., Vogt, J., Flagmeyer, R., Butz, T., 2000. Source identification of lead pollution in the atmosphere of Shanghai city by analyzing single aerosol particles (SAP). Environmental Science and Technology 34, 1900–1905.

Wang, W., Liu, X., Zhao, L., Guo, D., Lu, Y., 2003. Assessment of the phase-out of leaded gasoline in Tianjin, China using isotope technique. China Environmental Science 23 (6), 627–630 (in Chinese).

Winchester, J.W., Bi, M., 1984. Fine and coarse aerosol composition in an urban setting: a case study in Beijing, China. Atmospheric Environment 18, 1399–1409.

Wong, C.S.C., Li, X.D., 2004. Pb contamination and isotopic composition of urban soils in Hong Kong. The Science of the Total Environment 319, 185–195.

Ye, B., Ji, X., Yang, H., Yao, X., Chan, C.K., Cadle, S.H., Chan, T., Mulawa, P.A., 2003. Concentration and chemical composition of $PM_{2.5}$ in Shanghai for a 1-year period. Atmospheric Environment 37, 499–510.

Young, T.M., Heeraman, D.A., Sirin, G., Ashbaugh, L.L., 2002. Re-suspension of soil as a source of airborne lead near industrial facilities and highways. Environmental Science and Technology 36, 2484–2490.

Zhang, R., Wang, M., Zhang, W., Wang, Y., Li, A., Zhu, G., 2000. Research on elemental concentrations and distributions of aerosol in winter/summer in Beijing. Climatic and Environmental Research 5 (1), 6–12 (in Chinese).

Zhuang, G., Guo, J., Yuan, H., Zhao, C., 2001. The compositions, sources, and size distribution of the dust storm from China in spring of 2000 and its impact on the global environment. China Science Bulletin 46 (11), 895–901.

Zhuang, G., Guo, J., Yuan, H., Zhang, X., 2003. Coupling and feedback between Iron and sulphur in air–sea exchange. China Science Bulletin 48 (11), 1080–1086.