Atmospheric lead pollution in fine particulate matter in Shanghai, China

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Abstract

The Pb-monitoring program was extended for 6 years from 2002 to 2007 at 17 representative urban sites (6 traffic, 5 industrial, and 6 residential sites), and 3 suburban sites to assess the lead pollution in fine particulate matter ($PM_{2.5}$) after phasing out leaded gasoline in Shanghai. Compared with Pb levels reported in other places, the Pb pollution in Shanghai is still serious after phasing out leaded gasoline, which remains at high concentration range (213–176 ng/m³) in $PM_{2.5}$ in winter. Significant spatial variation of Pb concentrations and strong seasonal variation of higher Pb concentration in winter than that in summer were detected. The size distribution of Pb in particulate matter has a unimodal mode that peaks at approximately 0.154–1.59 μm particle diameter, indicating that Pb is mainly concentrated in fine fraction. Lead in the fine fraction is enriched by a factor of 10^3–10^4 relative to Pb abundance in crust. Eight categories of Pb pollution sources were identified in the $PM_{2.5}$ in the winter of 2007 in Shanghai. The important emission sources among them are vehicle exhaust derived from combustion of unleaded gasoline, metallurgic industry emission, and coal combustion emission.

Key words: atmospheric pollution; lead; pollution sources; X-ray analysis; single particle

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Introduction

Medical research has shown that Pb is a highly toxic element to human. The exposure to Pb will cause severe physiological or neurological effects even at low level, in particular for children (Fulton *et al*., 1987; Winneke *et al*., 1990). One of main pathways of Pb ingestion is by breathing air. Fine particulate matter $PM_{2.5}$ (particulate matter with aerodynamic diameter equal to or less than 2.5 μm) represents the main mass fraction of inhalable particulate matter PM_{10} (particulate matter with aerodynamic diameter equal to or less than 10 μm), which accounts for about 60% of PM_{10} mass. Fine particulate matter has long residence time in the atmosphere and can penetrate deeply into the lungs; thus, the toxicity of the fine particulate matter is higher than that of coarse airborne particles (Pacyna, 1995). Therefore, the pollution of atmospheric Pb as fine particulate matter has been paid much attention.

Lead added into gasoline as antiknock additives (tetraethyl and tetramethyl lead) was considered a major source of Pb contamination for a long time, and the maximal worldwide Pb contamination occurred in the middle of 1970s (Nriagu, 1989). However, until the end of 1970s, when its toxicity was realized, the atmospheric

lead concentrations in USA, Japan, and some countries in Europe first began to decrease due to the phase-out of leaded gasoline. For instance, atmospheric Pb concentration decreased from about 3000 ng/m³ in the early 1970s (Miller *et al*., 1972) to less than 10 ng/m³ in California in 1990s (Chow *et al*., 1996). In Shanghai, the use of leaded gasoline was stopped in 1997, and the Pb concentration in total suspended particles (TSP, particle matter with aerodynamic diameter equal to or less than 100 μm) decreased drastically from 3400 ng/m³ in 1995 to 400 ng/m³ in 2003 (Chen *et al*., 2005). However, the atmospheric Pb concentration is still high in Shanghai, with the average Pb concentration in PM_{10} (224 ± 45) ng/m³ (Tan *et al*., 2006), which still exceeded the air quality standard of Pb (200 ng/m³) recommended by the World Health Organization.

The studies on characteristics of atmospheric Pb in the fine particulate matter in Shanghai are rather limited, and there is little information available in literature about emission sources and size distributions of the atmospheric lead. Since 1998, our group has studied the atmospheric Pb pollution in Shanghai (Chen *et al*., 2005; Li *et al*., 2007; Tan *et al*., 2006; Wang *et al*., 2000a; Zheng *et al*., 2004). The atmospheric Pb pollution in coarse particles (TSP and PM_{10}) has been studied. Recently, Chen *et al*. (2008)

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suggested that the contribution from stationary industrial emissions to atmospheric Pb pollution of $PM_{2.5}$ is very substantial in Shanghai. For Pb pollution control, it is required to well understand characteristics and sources of the Pb in fine particulate matter. Therefore, a long-term monitoring of lead concentration in the $PM_{2.5}$ in Shanghai from 2002 to 2007 was conducted to evaluate characteristics and emission sources of the lead in $PM_{2.5}$.

1 Materials and methods

1.1 Sampling

$PM_{2.5}$ samples were collected from 20 sampling sites in Shanghai (Fig. 1), including Shangbo (SB), Jumen (JM), Kangpin (KP), Shisan (SS), Putuo (PT), Hongkou (HK), Pudong (PD), Shida (SD), Yangpu (YP), Taopu (TP), Huma (HM), Songnan (SN), Yanghang (YH), Gangyan (GY), Wusong (WS), Jiading (JD), Nanhui (NH), Minghang (MH), Qingpu (QP) and Chongming (CM). These sampling sites covered the urban and suburb of Shanghai, representing typical residential areas (KP, MH, PD, NH, TP and PT), industrial zones (YP, GY, SN, HM and YH), heavy traffic regions (JM, SB, SD, SS, HK and WS) and rural areas (QP, JD and CM). Due to the shirking of financial supports, the number sampling sites was reduced from 2005.

The $PM_{2.5}$ samples were collected in winter (January) and summer (July) from 2002 to 2007. Sampling duration was three weeks in January and July of each year. The climate of Shanghai is humid subtropical. The weather in Shanghai is under the influence of the Asian monsoon system. The ambient temperature is about 27.8 and 3.6°C and relative humidity (RH) is 75% and 83% as monthly average in July and January, respectively. The atmospheric pressure is higher in winter than in summer. The prevailing wind direction in winter is north, from northwest to northeast, and in summer is south, from south-east to southwest. The meteorological data in the sampling duration were downloaded from National Climate Data Center (http://cdc.cma.gov.cn).

TEOM2100 portable samplers (Rupprecht & Patashnick Co., Inc., USA) were used to collect $PM_{2.5}$ samples from the environmental monitoring sites. The $PM_{2.5}$ samples were collected on cellulose filters (Millipore Co., Ltd., USA, ϕ 47 mm, pore size 0.45 μm). The sampling flow rate was 5 L/min. The sampling site was about 12 m above the ground. Sampling time was 48 h for each sample. All those filers were weighed with an electronic balance (Sartorius BP211D, Max. 210g, reading precision 10 μg) after stabilizing in constant temperature ((20 ± 5)°C) and humidity (40% ± 2%).

A cascade impactor (DLPI, Dekat Ltd., Finland) was used to collect size-fractionated samples. It has 13 size-fractionated stages. The equivalent aerodynamic diameters of the 13 impactor stages are 0.0283, 0.0545, 0.0911, 0.154, 0.261, 0.380, 0.611, 0.945, 1.59, 2.38, 3.98, 6.47 and 9.92 μm. The size-fractionated samples were collected from sites GY, TP and JD in the winter of 2007. The sampling flow rate was 30 L/min. Sampling duration was 3–4 d at 12 m above the ground. The particulate matter was collected on polycarbonate membranes (Whatman Inc., UK, 25 mm). All those filers were weighed with an electronic balance (Gibertini Crystal 250, Max. 5 g, reading precision 1 μg) after stabilizing in constant temperature ((20 ± 5)°C) and humidity (40% ± 2%).

Thirty three samples from possible emission sources were collected. These sources are metallurgic emissions (including converter for steelmaking, electric furnace for steelmaking, coke oven and sintering plant), coal combustion (including coal-fired power plants and coal-fired boilers), cement dust, soil dust and vehicle exhaust (including combustions of leaded gasoline and unleaded gasoline).

1.2 Proton induced X-ray emission analysis

The proton induced X-ray emission (PIXE) technique was used to analyze lead in $PM_{2.5}$ samples at the Nuclear Analysis Laboratory in Shanghai Institute of Applied Physics. The 3.5 MeV proton beam was generated by a Van de Graaff accelerator. The proton beam was diffused by a thin aluminum foil (6.7 mg/cm^2) and finally collimated to a beam spot of 6 mm diameter on the sample target. Typical beam current was 10–20 nA. The average measuring time per sample was 30 min. The X-rays were detected with a Si(Li) detector with an energy resolution of 160 eV at 5.9 keV (Mn K_α line). The detector was located at 135° with respect to the proton beam direction in the horizontal plane. PIXE spectra were analyzed by the AXIL software package (QXAS 3.6). A set of micro-matter standard reference samples (Micromatter Co., USA) was used for the calibration of the analytical system. Detection limit was less than 1 ng/m^3 for lead. No signification contamination was detected in the analysis of blank filters. The detail of the PIXE analyses has been described elsewhere (Zhang *et al.*, 2006).
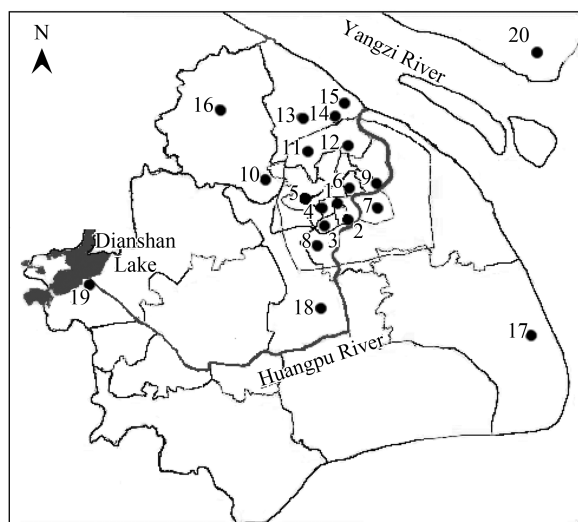

Fig. 1 Locations of the sampling sites in Shanghai. (1) SB; (2) JM; (3) KP; (4) SS; (5) PT; (6) HK; (7) PD; (8) SD; (9) YP; (10) TP; (11) HM; (12) SN; (13) YH; (14) GY; (15) WS; (16) JD); (17) NH; (18) MH; (19) QP; (20) CM.

1.3 Inductively coupled plasma mass spectrometer analysis

The particulate matter collected by the DLPI cascade impactor are distributed as many spots on polycarbonate membranes. Due to the limitation of PIXE analysis, the inductively coupled plasma mass spectrometer (ICP-MS, X-7 Model, Thermo-Elemental Inc., England) was used to analyze lead in the size-fractionated samples at the Nuclear Analysis Laboratory in Shanghai Institute of Applied Physics. The polycarbonate membranes were digested at 170°C for 40 min in a high-pressure microwave digestion system (Ethos 320, Milestone, Italy) with concentrated acid mixture (3 mL HNO_3, 1 mL HCl and 1 mL HF). The resulting solutions were dried in PTFE beakers and then diluted to 10 mL with deionized water (> 18 MΩ, produced by Millipore Milli-Q purifier). Thallium standard solution was added to sample solutions as an internal standard, and the certified standard solution of Pb (1000 μg/mL, SPEX CertiPrep Inc.) was used to prepare calibration solutions. The ICP-MS instrument was operated at high-performance interface configuration. The radio frequency power of 1250 W was applied to the plasma. Flow rates of cool, auxiliary and nebulizer gases were 14, 0.7 and 0.85 L/min, respectively. Blank solutions were also prepared with unexposed polycarbonate membranes in parallel. The blank lead concentration was lower than 0.01 ng/mL, which could be neglected in this work.

1.4 Synchrotron X-ray fluorescence microprobe analysis

In this work, individual particle analysis was applied to source identification of lead-containing particles in $PM_{2.5}$ in Shanghai. Synchrotron X-ray fluorescence microprobe (μ-SXRF) was used for the individual particle analysis at Photon Factory in High Energy Accelerator Research Organization, Japan. The electron energy and ring current of the synchrotron light source were 2.5 GeV and 310–430 mA, respectively. The 17.4 keV monochromatic X-ray was used to excite samples for the determination of trace lead in individual $PM_{2.5}$ particles. The monochromatic X-ray beam was focused by a Kirkpatric-Baez optics, offering square beam spot of 5 μm × 5 μm. The photon flux of the monochromatic X-ray microbeam at the sample position was about 5×10^9 photon/(s·300 mA) under the beam spot size. A Si(Li) semiconductor detector was applied to detect characteristic X-rays. The energy resolution of the Si(Li) detector was 133 eV at 5.9 keV (Mn K_α line). The $PM_{2.5}$ particles on films were randomly chosen in the analysis. Irradiation time was 60 s for each $PM_{2.5}$ particle. The details of the μ-SXRF analysis have been described elsewhere (Li *et al.*, 2007b).

For quality control (QC) of Pb analyses, a standard reference material issued by National Institute of Standards and Technology of USA, NIST1648 (airborne particles), was analyzed by PIXE and ICP-MS in parallel. The analytical results of Pb in NIST1648 ((6530 ± 30) μg/g) agree well with Pb standard value ((6550 ± 80) μg/g) of the standard reference material, indicating that the Pb analyses

are reliable in this work. In the Pb source apportionment, a method combining μ-SXRF spectra of individual airborne particles with pattern recognition technique was used to directly identify the sources of lead-containing particles. Thus, the apportionment method avoids quantitative analysis of Pb in μ-SXRF.

2 Results and discussion

2.1 Lead concentration in Shanghai air

The Pb concentrations at 20 monitoring sites in Shanghai from 2002 to 2006 are presented in Table 1. The average concentrations of Pb ranged from 213 to 176 ng/m^3 in the winter from 2002 to 2006. The highest average concentration of Pb (283 ng/m^3) was observed at site HM within the steel industrial zone. Even in the summer of 2004, 2005 and 2006, Pb average concentration is high up to 61–91 ng/m^3. In the early 1990s, low Pb concentration of 1–11 ng/m^3 in $PM_{2.5}$ was detected in the central California (Chow *et al.*, 1996). Recent investigation in 20 large cities of USA showed that the annual average concentration of Pb in $PM_{2.5}$ was 25 ng/m^3 during 2003–2005 (USEPA, 2007). A study of $PM_{2.5}$ in Hong Kong reported the Pb concentrations of 76.9 and 91.6 ng/m^3 at traffic site and industrial site, respectively (Ho *et al.*, 2003). The low Pb concentrations in $PM_{2.5}$ was detected at a traffic site in Taichung in Taiwan in the winter of 2000 (34 ng/m^3) (Fang *et al.*, 2002) and in Helsinki in Finland (5.8 ng/m^3) (Pakkanen *et al.*, 2001). Compared with these reported data, the atmospheric Pb pollution in Shanghai is still serious after phasing out leaded gasoline.

Lead concentrations in $PM_{2.5}$ showed a significant spatial variation in Shanghai (Table 1). The average Pb concentrations range from 283 to 140 ng/m^3 in heavy traffic areas and metallurgic industry zones. The average Pb concentrations at residential areas are ranged from 107 to 83 ng/m^3. Except JD site, the rural sites in suburb have average Pb concentrations range 76–32 ng/m^3. The lowest Pb concentration of 8.5 ng/m^3 was observed at CM site in the summer of 2007. This spatial variation suggests that the metallurgic industry and traffic actions are the major emission sources of atmospheric Pb. For the high average Pb concentration at JD site, the possible reason is that as the rapid expansion of the city zone of Shanghai, more traffic activity has been introduced and some metallurgic plants moved into the areas around JD.

As one of the largest city in China, Shanghai has been paid much attention to its air quality. Since metallurgic activities have been considered as air pollution sources, some effective methods have been taken by local government to reduce the emissions of metallurgic factories. Some old steel plants with high emission of pollutant were closed in past six years. Thus, the air quality was improved, and the Pb concentrations decreased at some monitoring sites (Fig. 2a). For instance, after the Shanghai Fifthly Steel Plant in the neighborhood of GY site was closed, the Pb concentration at GY site evidently decreased. However, most of sites did not show significantly degressive trends

Table 1 Lead concentration in $PM_{2.5}$ in Shanghai (ng/m^3)

Sampling site	Environ. type	2002 winter	2003 winter	2004 winter	2004 summer	2005 winter	2005 summer	2006 winter	2006 summer	Mean	SD	RSD (%)
HM	Steel	295 ± 8	338 ± 30	373 ± 56	163 ± 10	245 ± 29				283	82	29
GY	Steel	650 ± 41	477 ± 36	266 ± 29	78 ± 5	358 ± 31	63 ± 6	89 ± 8	134 ± 11	264	216	82
SN	Steel	285 ± 6	377 ± 41	201 ± 23	72 ± 5	359 ± 38		337 ± 22	176 ± 15	258	113	44
YH	Steel	280 ± 15	166 ± 14	199 ± 21	129 ± 15	302 ± 25				215	74	34
YP	Metal.	510 ± 24	439 ± 52	233 ± 25	98 ± 10	147 ± 13	21 ± 2.1			241	195	81
JM	Traf.	327 ± 11	303 ± 26	453 ± 68	136 ± 16	230 ± 33	76 ± 8			254	137	54
SB	Traf.	408 ± 14	217 ± 22	97 ± 13	24 ± 2	158 ± 11	73 ± 7			163	138	85
SS	Traf.	56 ± 3	226 ± 27	141 ± 16	110 ± 10	332 ± 29		245 ± 28	30 ± 6	159	111	70
HK	Traf.	116 ± 10	130 ± 12	124 ± 16	63 ± 4	338 ± 34				154	106	69
SD	Traf.	156 ± 7	151 ± 13	354 ± 46	35 ± 3	114 ± 14	52 ± 3			144	115	80
WS	Traf.	255 ± 13	141 ± 11	143 ± 26	75 ± 5	85 ± 6				140	72	51
KP	Resid.	57 ± 3	80 ± 7	302 ± 48	14 ± 2	84 ± 7				107	112	104
NH	Resid.	175 ± 7	98 ± 10	112 ± 17	77 ± 5	75 ± 8				107	41	38
TP	Resid.	55 ± 4	157 ± 13	141 ± 27	94 ± 10	59 ± 4				101	46	46
MH	Resid.	75 ± 5	100 ± 9	241 ± 32	12 ± 1	64 ± 6				98	86	87
PD	Resid.	169 ± 11	29 ± 2	90 ± 12	37 ± 2	189 ± 22	48 ± 4			93	69	74
PT	Resid.	52 ± 2	72 ± 8	90 ± 11	42 ± 3	133 ± 15	86 ± 7	147 ± 17	41 ± 6	83	40	48
JD	Rural	85 ± 3	126 ± 14	97 ± 13	82 ± 7	79 ± 9	68 ± 4	180 ± 21	158 ± 17	109	41	38
QP	Rural	46 ± 3	88 ± 9	113 ± 18	77 ± 5	71 ± 8	63 ± 4			76	23	30
CM	Rural							56 ± 3	8.5 ± 4	32	34	104
Mean		213	196	194	78	180	61	176	91			
SD		171	131	113	43	111	19	103	73			
RSD (%)		80	67	58	55	62	31	59	80			

Steel: steel industrial zones; metal.: metallurgic factories; traf.: heavy traffic regions; resid.: residential areas; rural: rural areas in suburb.

in Pb levels (Fig. 2b). This means that there still are many Pb sources working in Shanghai. Therefore, the further cut down of Pb emission sources for improving the air quality of Shanghai is still needed.

Seasonal variation of Pb concentrations in $PM_{2.5}$ in Shanghai was monitored (Fig. 3). The Pb concentrations in winter are significantly higher than those in summer. This result is in agreement with Sun et al., (2006) who reported that the concentrations of Pb in winter were higher than those in summer in $PM_{2.5}$ in Beijing. They concluded that the higher concentrations of Pb in winter were likely attributed to the much higher consumption of coal for heating rooms in this season, and the higher emission of exhaust due to the incomplete combustion of fuel in cold season. However, it seems that their explanation does not fit the case of Shanghai. Compared to the lowest monthly average ambient temperature in Beijing (–15°C), the lowest value 3.6°C in Shanghai can not cause a such high consumption of coal for heating rooms in winter. The higher concentrations of Pb in Shanghai in winter are likely attributed to its meteorological condition and location

of steel industry zone. In summer, a higher wind speed and ambient temperature (the highest monthly average of 27.8°C) favor the air convection and dispersion of pollutants. Whereas, the low wind speed and low ambient temperature in winter favor the accumulation of pollutants. Moreover, as a coastal city, the prevailing wind direction in summer is from southeast to southwest in Shanghai. Thus, the cleanly southeast wind from East China Sea and Pacific Ocean in summer dilutes the air pollutants and blows away the industrial pollutants derived from the steel industry zone located in North Shanghai. Whereas, the prevailing wind direction is north, from northwest to northeast in Shanghai in winter, which bring pollutants from inland and the steel industry zone to the downwind zone of Shanghai. Therefore, the Pb concentrations in winter are observably higher than those in summer.

2.2 Size distribution of lead in particulate matter in Shanghai

Knowledge of the size distribution of Pb in particulate matter is essential in understanding the sources of
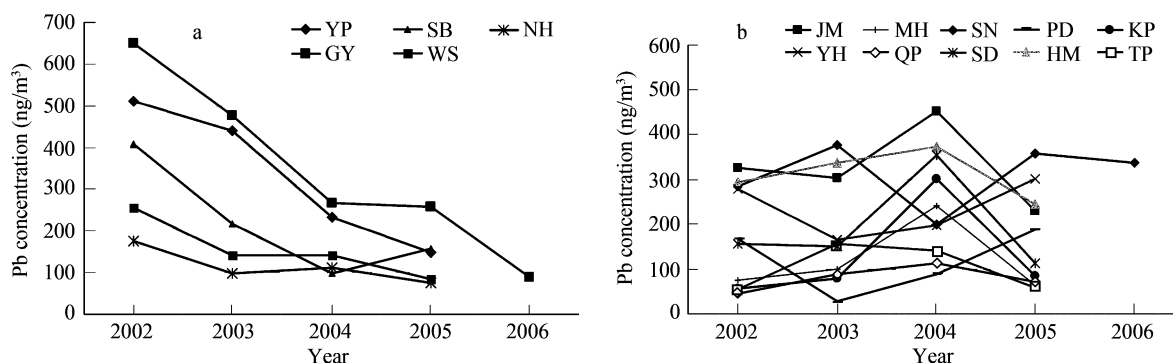

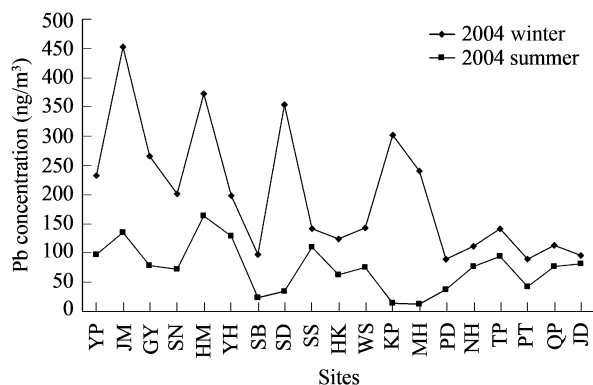**Fig. 2** Variations of Pb concentrations at monitoring sites in Shanghai in the winter from 2002 to 2006.

Fig. 3 Seasonal variation of Pb concentration in Shanghai.

atmospheric Pb and its effect on human health. To study characteristics of size distribution of atmospheric Pb, a cascade impactor (DLPI, Dekat Ltd., Finland) was used to collect particulate matter in Shanghai.

The size-fractionated samples were collected at sites JD (rural area in suburb), GY (steel industry zone) and PT (residential areas) in the winter of 2007. The size distributions of particulate matter at the sites are characterized by bimodal mode (Fig. 4a). Two peaks are in ranges of 0.154–1.59 μm and 1.59–3.98 μm particle diameter, respectively. The average mass fraction of the fine particles (particle diameter < 1 μm) is about 60%. The result shows that the fine particles were dominate at the sites.

In contrast, the size distributions of Pb in particulate matter at these sites are characterized by unimodal mode that peaks at approximately 0.154–1.59 μm particle diam-

eter (Fig. 4b). The Pb is mainly (over 80%) concentrated in the fine fraction (particle diameter ⩽ 1 μm), which is usually from anthropogenic sources, such as vehicle exhaust and industrial activities (Sun *et al.*, 2006), and can enter the human body easily.

Enrichment factor (EF) is usually applied to assess the strength of pollution sources in relation to crustal sources (Xu *et al.*, 2007). In order to evaluate Pb emission sources in Shanghai, the EFs of Pb in the size-fractionated samples were calculated:.

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

where, Al is the reference element of crustal material. $(Pb/Al)_{air}$ and $(Pb/Al)_{crust}$ are the concentration ratios of Pb to Al in the airborne particles and crust, respectively. The abundances of Al and Pb in the earth crust were taken from reference (Wedepohl, 1995). The calculation results show that the EFs of all size-fractionated samples at the sites are much higher than 10, and that the lead in the fine fraction (0.945–0.0911 μm) is enriched by a factor of 10^3–10^4 relative to Pb abundance in crust (Table 2). The high EFs, especially in the fine particles, indicate that the Pb is originated from anthropogenic sources.

Zereini *et al.* (2005) indicated that the average atmospheric residence time of fine particles (0.1–2 μm) is 3–7 d and metals bounded to the fine particles can be transported over long distances before they return to the ground. Moreover, although the concentrations of particulate matter and atmospheric lead at JD site are significantly lower than those at GY and PT sites, the patterns of size distributions of particulate matter and atmospheric lead are similar at those sites (Fig. 4). Therefore, it can be concluded that the Pb emitted from traffic and steel industrial activities diffused to rural area of Shanghai. In addition, the EFs at site JD in all particle sizes are significantly higher than those at GY and PT (Table 2). This means that there must be another source with high Pb concentration, which has contribution to the high EFs value in JD site.

2.3 Sources identification

Wang *et al.* (2000b) revealed that individual airborne particles from different emission sources have different elemental compositions, which can be characterized by their characteristic X-ray spectra. In our earlier study, pattern recognition (PR) system has been developed to

Table 2 Enrichment factors of lead in 13 size-fractionated samples at sites JD, GY and PT

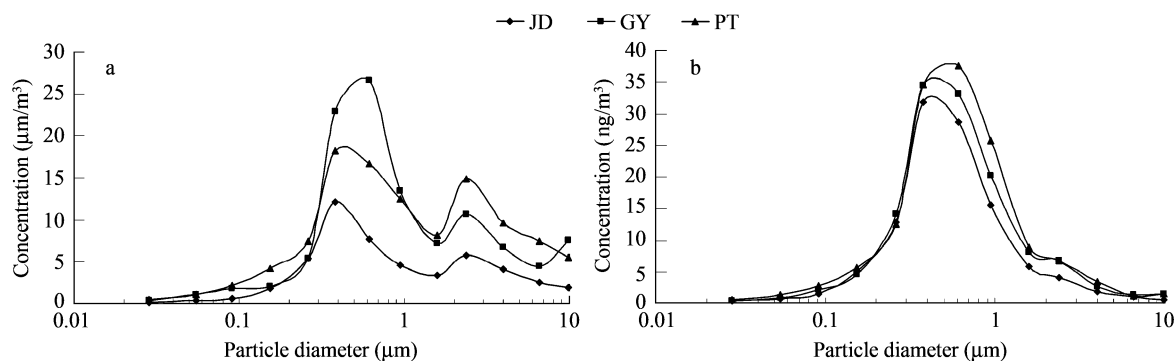| Particle diameter (μm)	JD	GY	PT
> 9.92	50	38	34
9.92–6.57	65	40	38
6.57–3.98	73	54	33
3.98–2.38	122	84	50
2.38–1.59	365	235	143
1.59 –0.945	1393	781	715
0.945–0.611	4923	2320	2891
0.611–0.380	10130	4759	4366
0.380–0.261	14144	3634	5094
0.261–0.154	17356	2071	3075
0.154–0.0911	1285	727	1456
0.0911–0.0545	114	417	1462
0.0545–0.0283	746	127	132

Fig. 4 Size distributions of particulate matter (a) and atmospheric Pb (b).

direct recognize sources of the individual airborne particles by their characteristic X-ray spectra (Guo *et al.*, 2000). By comparing the μ-SXRF spectra of the environmental monitoring samples with those in the fingerprint library of the emission sources by using the PR system, the sources of the individual airborne particles from the atmospheric environment can be directly identified (Yue *et al.*, 2004; Li *et al.*, 2007b). In this work, the individual particle analysis based on the μ-SXRF technique was applied to source identification of Pb-containing PM$_{2.5}$ particles in Shanghai. The detail of the source apportionment method using individual particle analysis has been described elsewhere (Li *et al.*, 2009).

Four PM$_{2.5}$ samples were collected at SB (heavy traffic area), PT (residential areas), GY (steel industry zone) and JD (rural site in suburb) sites in the winter of 2007. About one thousand individual fine particles from these samples were analyzed by the μ-SXRF. The source apportionment of lead was performed using the source apportionment method. Eight categories of Pb emission sources are shown in Fig. 5.

The contribution of vehicle exhaust from combustion of unleaded gasoline is the highest (47.1%–63.1%), suggesting that the Pb emission from automobiles may be still a main source of the lead pollution in Shanghai. Unleaded oil fuels still contain lead, which might originate from the crude oil. Tan *et al.* (2006) also detected the unignorable average lead concentration of (238 ± 5) μg/g in the vehicle exhaust. There are over 2 million motor vehicles in Shanghai. Annual consumption of oil fuels was about 6.2 million tons in Shanghai in 2006 (http://yxj.ndrc.gov.cn/dfyx/t20070514_134768.htm). Due to vast consumption of oil fuels, even low Pb concentration in oil fuels could make a significant contribution to the total emission of atmospheric Pb.

After the use of leaded oil fuels was stopped in Shanghai in 1997, the number of aerosol particles from combustion of leaded gasoline was decreased from 18% in 1999 (Wang *et al.*, 2000a) to a few in 2002, till no particle was detected in current study. This implies that the environmental impact from the combustion of leaded gasoline would be efficiently reduced in Shanghai after 10 years of phasing out leaded gasoline.

The contribution of metallurgical activities is the second highest emission source at the monitoring sites. They are 41.2%, 35.9%, 20.7% and 19.0% (sum of emissions from converter for steelmaking, electric furnace for steelmaking, coke oven and sintering plant) at SB, PT, GY and JD, respectively (Fig. 5). The high contribution of metallurgical activities implies that the Pb emission from metallurgical industry may be an important source of lead pollution in Shanghai. This may be attributed to steel industry of Shanghai. For example, the biggest metallurgic complex in China, the Baosteel Group, is located in the north of Shanghai. As a result, the higher Pb contribution from the steel industry was observed at SB and PT located in the downwind area of the steel industrial zone in winter.

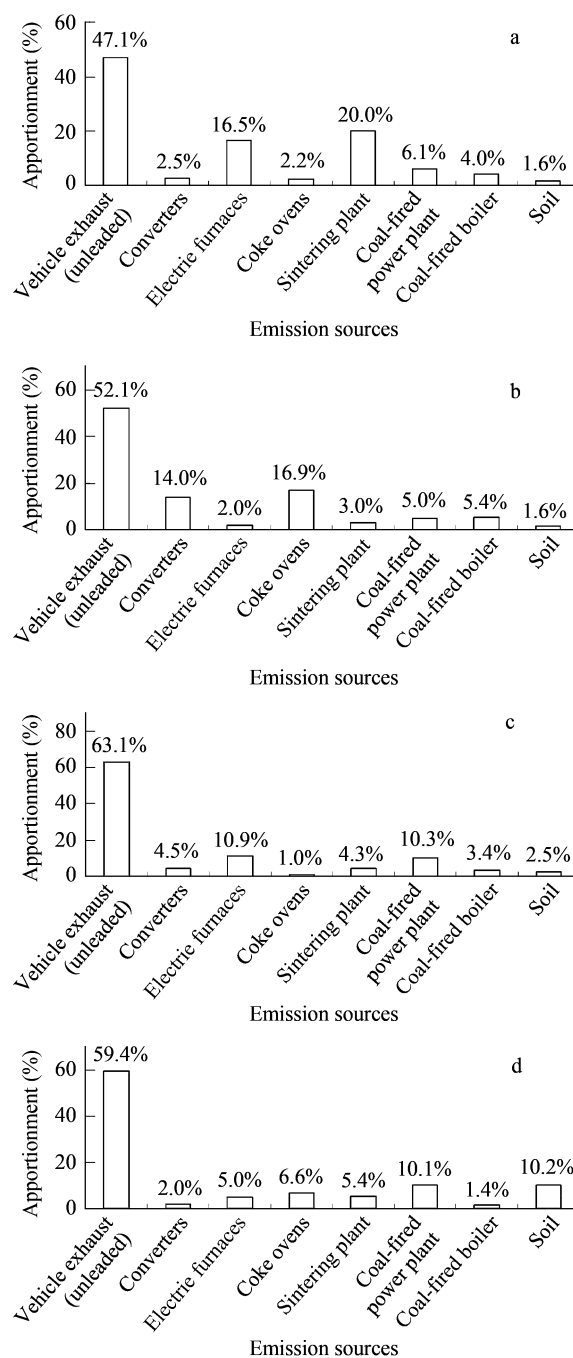The over 10% contribution of coal combustion at each site (sum of emissions from coal-fired pow-

Fig. 5 Source apportionment of lead in PM$_{2.5}$ particles collected at sites SB (a), PT (b), GY (c) and JD (d) in the winter of 2007.

er plants and coal-fired boilers) is due to some large coal-fired power plants and many coal-fired boilers in Shanghai. Annual consumption of coal was about 52 million tons in Shanghai in 2006 (http://yxj.ndrc.gov.cn/dfyx/t20070514_134768.htm), and annual output of the soot was vast. The Pb concentrations in coal are low, which range from 13 to 86 μg/g (Zheng *et al.*, 2004), but Pb concentration in coal combustion ash is high up to (1788 ± 37) μg/g (Tan *et al.*, 2006). Therefore, the Pb emission from combustion of coal cannot be ignored.

In this study, the contribution from soil and cement dust caused from uncovered ground surface, municipal

construction sites and building construction sites is not significant except site JD. The contribution of soil dust is under 3% at sites SB, PT and GY, and no cement particles were detected. This may be attributed to large-scale tree and grass planting and setting of dustproof enclosures in the construction sites in Shanghai. The reason for the high contribution of soil dust (10.2%) at site JD, located in a rural area in suburb of Shanghai, is that there are bare farmlands in winter.

3 Conclusions

The Pb pollution in $PM_{2.5}$ in Shanghai has been serious after phasing out leaded gasoline, which remains in high level (213–176 ng/m^3) in the $PM_{2.5}$ in winter. There are significant spatial and seasonal variations of Pb concentrations in Shanghai air. The size distribution of atmospheric Pb shows that the atmospheric Pb is mainly concentrated in fine fraction. The Pb in fine fraction is enriched by a factor of 10^3–10^4 relative to Pb abundance in crust. The important emission sources of atmospheric Pb in Shanghai are vehicle exhaust derived from combustion of unleaded gasoline, metallurgic industry emission and coal combustion emission.

Acknowledgments

References

Chen J M, Tan M G, Li Y L, Lu W, Tong Y P, Zhang G L, Li Y, 2005. A lead isotope record of Shanghai atmospheric lead emissions in total suspended particles during the period of phasing out of leaded gasoline. *Atmospheric Environment*, 39: 1245–1253.

Chen J M, Tan M G, Li Y L, Zheng J, Zhang Y, Shan Z *et al.*, 2008. Characteristics of trace elements and lead isotope ratios in $PM_{2.5}$ from four sites in Shanghai. *Journal Hazardous Materials*, 156: 36–43.

Chow J C, Waston J G, Lu Z, Lowenthal D H, Frazier C A, Solomon P A *et al.*, 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, Yang C J, Chen C D *et al.*, 2002. Ambient suspended particulate matter and related chemical species study in central Taiwan, Taichuang during 1998–2001. *Atmospheric Environment*, 36: 1291–1298.

Fulton M, Thomson G, Hunter R, Raab G, Laxen D, Hepburn W, 1987. Influence of blood lead on the ability and attainment of children in Edinburgh. *The Lancet*, 329: 1221–1226.

Guo P, Wang J, Li X, Zhu J, Reiner T, Heitmann J *et al.*, 2000. Combination of micro-PIXE with the pattern recognition technique for the source identification of individual aerosol particles. *Applied Spectroscopy*, 54(6): 807–811.

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.

Li X L, Bao L M, Liu J F, Yue W S, Li Y, Zhang G L, 2007a. Source identification of single lead-containing particles in the ambient air of Shanghai City in winter 2004. *Journal of Graduate School of the Chinese Academy of Sciences*, 24(5): 688–691.

Li X, Yue W, Iida A, Li Y, Zhang G, 2007b. A study of the origin of individual $PM_{2.5}$ particles in Shanghai air with synchrotron X-ray fluorescence microprobe. *Nuclear Instruments and Methods in Physics Research B*, 260: 336–342.

Li X L, Zhang G L, Li Y, 2009. A method for source apportionment of lead in fine particulate matter based on individual particle analysis using a synchrotron X-ray fluorescence microprobe. *Applied Spectroscopy*, 63(2): 180–184.

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

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

Pacyna J M, 1995. The origin of Arctic air pollutants: lessons learned and future research. *Science of the Total Environment*, 160/161: 39–53.

Pakkanen T A, Loukkola K, Korhonen C H, Aurela M, Makela T, Hillamo R E *et al.*, 2001. Soueces and chemical compositions of atmospheric fine and coarse particles in the Helsinki area. *Atmospheric Environment*, 35: 5381–5391.

Sun Y L, Zhuang G S, Zhang W J, Wang Y, Zhuang Y H, 2006. Characteristics and sources of lead pollution after phasing out leaded gasoline in Beijing. *Atmospheric Environment*, 40: 2973–2985.

Tan M G, Zhang G L, Li X L, Zhang Y X, Yue W S, Chen J M *et al.*, 2006. Comprehensive study of lead pollution in Shanghai by multiple techniques. *Analytical Chemistry*, 78: 8044–8050.

USEPA (U.S. Environmental Protection Agency), 2007. Review of the National Ambient Air Quality Standards for Lead. EPA-452/R-07-013.

Wang J, Guo P, Li X, Zhu J, Reiner T, Heitmann J *et al.*, 2000a. Source identification of lead pollution in the atmosphere of Shanghai city by analyzing single aerosol particles (SAP). *Environmental Science & Technology*, 34: 1900–1905.

Wang J, Guo P, Li X, Zhu J, Reiner T, Heitmann J *et al.*, 2000b. Identification of air pollution sources by single aerosol particle fingerprints – micro-PIXE spectra. *Nuclear Instruments and Methods in Physics Research B*, 161-163: 830–835.

Wedepohl K H, 1995. The composition of the continental crust. *Geochimica et Cosmochimica Acta*, 59: 1217–1232.

Winneke G, Brockhaus A, Ewers U, Krämer U, Neuf M, 1990. Results from the European multicenter study on lead neurotoxicity in children: implications of for risk assessment. *Neurotoxicol Teratol*, 12: 553–559.

Xu H H, Wang Y S, Wen T X, He X X, 2007. Size distributions and vertical distributions of metal elements of atmospheric aerosol in Beijing. *Environmental Chemistry*, 26(5): 675–679.

Yue W S, Li Y, Li X L, Yu X H, Deng B, Liu J F *et al.*, 2004. Source identification of PM_{10}, collected at a heavy-traffic roadside, by analyzing individual particles using synchrotron radiation. *Journal of Synchrotron Radiation*, 11: 428–431.

Zereini F, Alt F, Messerschmidt J, Wiseman C, Feldmann I, Bohlen A V *et al.*, 2005. Concentration and distribution of heavy metals in urban airborne particulate matter in Frankfurt am Main, Germany. *Environmental Science & Technology*, 39: 2983–2989.

Zhang Y X, Zhang Y M, Wang Y S, Li D L, Li A G, Li Y *et al.*, 2006. PIXE characterization of PM_{10} and $PM_{2.5}$ particulate matter collected during the winter season in Shanghai City. *Journal of Radioanalytical and Nuclear Chemistry*, 267: 497–499.

Zheng J, Tan M G, Shibata Y, Tanaka A, Li Y, Zhang G L *et al.*, 2004. Characteristics of lead isotope ratios and elemental concentrations in PM_{10} fraction of airborne particulate matter in Shanghai after the phase-out of leaded gasoline. *Atmospheric Environment*, 38: 1191–1200.

Zhu G H, Wang G F, Zhang R J, 2004. Characteristic variations of atmospheric particles in Beijing. *The Chinese Journal of Process Engineering*, 4 Suppl.: 717–720.