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Characteristics of trace elements and lead isotope ratios in PM$_{2.5}$ from four sites in Shanghai

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Abstract

PM$_{2.5}$ samples were collected in Shanghai at four sites with different typical land-uses. The sampling was done concurrently once per month from April 2004 to April 2005, and the ambient mass concentration, the elemental composition and the stable lead isotope ratios in these PM$_{2.5}$ samples were determined. The annual average concentrations of PM$_{2.5}$ samples at each site were 84 ± 30, 65 ± 20, 55 ± 18, and $41 \pm 10\,\mu g\,m^{-3}$, respectively, indicating there were severe air pollution levels in Shanghai. The enrichment factor was calculated for each element and the comparison and discussion of elements with significant anthropogenic contributions between Shanghai and Tokyo suggested that the major source of PM$_{2.5}$ in Shanghai was not traffic-derived emissions, but the stationary industrial contribution emitted from coal use. Moreover, the analysis of stable lead isotope ratios revealed only a slight difference within the samples at the four sites which fell well within the scope of coal composition difference, further confirming that the contribution from stationary industrial emissions to atmospheric lead pollution of PM$_{2.5}$ was very substantial in Shanghai.
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Keywords: Fine particulate matters; Mass concentration; Elemental composition; Enrichment factor; Lead isotope ratio

1. Introduction

Shanghai is the largest city in China with a population of 18 million in 2004. Located in east China at the mouth of the Yangtze River, the city has many industrial developments, which include the world's largest seaport, and the largest petrochemical, iron and steel, and car-making complexes in China. In recent years, owing to rapid industrial and social developments, Shanghai is facing a serious challenge of air pollution problem, of which particulate matter has been frequently emerged as key pollutants of concern reported daily by Shanghai Environment Monitoring Center (SEMC), caused by various anthropogenic

sources, such as coal-combustion-based power industry and heavy transportation of road vehicles, etc. Fine particulate matter (with aerodynamic diameter less than 2.5 μm, and designated as PM$_{2.5}$) has drawn worldwide attention for its adverse impact on human health and a growing body of evidence from epidemiologic studies has indicated that there is a strong link between elevated ambient concentrations of PM$_{2.5}$ and increased mortality and morbidity [1–3].

Conventionally, vehicular emissions are generally viewed as the major sources of ultrafine and fine particles in urban environment, particularly in terms of lead pollution. However, that does not seem to be the case in Shanghai. The introduction of unleaded gasoline began early in the 1990s and the consumption of leaded gasoline was officially banned in 1997. However, extraordinarily high atmospheric lead concentrations with a mean value of 515 ng m^{-3} were still present in Shanghai in 2001 after years of phasing out leaded gasoline [4]. According to reported information for the past two decades, the contribution from automotive

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emissions to airborne lead was always surprisingly low in Shanghai with respect to other emission sources [4–7]. The authors' previous studies revealed that instead of gasoline combustion, the long-time use of coal for China's accelerated industrialization was the primary contributor to airborne lead pollution [7,8]. Xiu et al. [9] measured major water-soluble inorganic ions in size-fractionated PM and proved that stationary source emission was the predominant contributor to fine particles. Moreover, it has also been reported that stationary emissions were always the dominant source of PM$_{2.5}$ in Shanghai [10,11]. These findings have all provided valuable insights for planning future monitoring and energy policy making studies.

A number of studies conducted in Shanghai during the last two decades have dealt with mass concentration levels, seasonal variations, chemical compositions, major sources, size distributions, and the existing forms of major ions [4–13]. Relatively high levels of ambient PM have been well documented in Shanghai [4,7,8,10–13], and the emission inventory and the source apportionment by chemical speciation are the basic tools supporting the control policy. Thus, in order to expand on previous information about the PM$_{2.5}$ presence in urban areas and to have a better understanding of the problem, a more reliable assessment focusing on the role of stationary source emissions in the greater Shanghai area should be very helpful.

In this work, a standardized monitoring network was set up to complement some previous findings; particular focus was placed on the role of stationary source emissions, other than mobile sources. Taking the predominant land-use as the selection criterion, PM$_{2.5}$ aerosol samples were concurrently collected for a 1-year period at four sites in Shanghai. The sampling campaigns were set to allow the direct comparison of the spatial distribution of PM$_{2.5}$ mass concentrations and chemical characteristics of trace elements, in a bid to elucidate the source processes governing the behavior of PM$_{2.5}$ pollution. Since the global emission of lead in urban environments has increased significantly due to the combustion of leaded gasoline, the stable lead isotope ratios in collected airborne particle samples were also investigated in an effort to better interpret the relationship between the anthropogenic industrial contribution and the local traffic-derived contribution.

2. Experimental

2.1. Aerosol sampling

The four PM$_{2.5}$ sampling sites were selected according to different patterns of anthropogenic activities in Shanghai registered by SEMC. They included a control site, an industrial site, an urban residential site and an urban commercial site (Fig. 1). PM$_{2.5}$ measurements were carried out concurrently at the four sampling locations. The control site samples were collected on the rooftop of the Key Laboratory of Nuclear Analysis Techniques building in Shanghai Institute of Applied Physics (SINAP), Chinese Academy of Sciences in Jiading district (Jiading). SINAP is a research institute with no commercial or industrial activities. The institute which is largely covered with evergreen trees lies at about 40 km northwest of the downtown

Fig. 1. Map of Shanghai showing the study area and main roads. Four sampling locations are indicated as follows: Jiading-rural/background, Putuo-urban/residential, Huangpu-urban/commercial, Baoshan-suburban/industrial.

town and is surrounded by farmland. This selection as the control allowed recording of the ambient background of pollutants in a suburban area. Samples obtained for the other three sites were collected at the rooftop of the SEMC air quality monitoring stations of each location. The industrial site (Baoshan), located in the northeast part of Shanghai, is a well-known steel manufacturing area. This area continuously has high air pollution levels as a consequence of contaminated fumes and effluents from local industries. The urban residential site (Putuo) is located about 25 km southwest of the Baoshan industrial area. Numerous commercial activities and heavy traffic use are found in and around this area, which is typical of a large city. The urban commercial site (Huangpu), which located a little bit far away than Putuo in the same direction, also experiences heavy traffic use throughout the day. The sampling heights were from 15 to 20 m above the ground which prevented interferences from the vertical dispersion of primary airborne PM emitted from sources close to the ground surface, such as vehicle exhaust and soil re-suspension dust, excluding exceptional concentrations.

Four sets of medium volume rate air samplers were employed to collect PM$_{2.5}$ samples (Model-2, Beijing Geological Instrument Factory, China). The airflow rate of each sampler was calibrated and controlled uniformly at 0.080 m^3 min^{-1}. In addition, the exact sampled air volumes were recorded by air-flow meters for quality assurance. Reasonably good agreement was observed between the air samplers. Operation of the air samplers in the manner proposed minimized the discrimination effect of the sampling efficiency between samplers and should be capable of accurate estimating of PM loading. Sampling was done from April 2004 to April 2005. Sample collection began usually at 9:00 a.m. and samplings were carried out continuously for 24 h once per month. Air quality and meteorological data were recorded simultaneously by the SEMC at the monitoring stations. Acid cleaned Teflon membrane filters (PTFE, 86 mm

effective diameter, Millipore, USA) were used for the collection of aerosol particles. All filters were double bagged before and after sampling to prevent contamination. A total of 13 sets of samples were obtained at each site and a field operational blank sample was also conducted at each site.

2.2. Analysis and quality assurance

PM$_{2.5}$ masses were determined by gravimetry. Before and after the sampling, the Teflon membrane filters were weighed on an analytical balance with a reading precision of 0.01 mg. The samples were allowed to reach humidity equilibrium in the weighing room for 24 h before weighing. The relative humidity and temperature in the weighing room were $50 \pm 6\%$ and $23 \pm 2 °C$, respectively. The weight of collected PM$_{2.5}$ samples loaded on the filter ranged from 2.71 to 27.56 mg, averaging 7.81 ± 4.75 mg. After weighing, the samples were conditioned in a desiccator until chemical analysis.

Particle loaded filters, including the field blank, were appropriately cut using a special round hand punch made of high purity molybdnum. Duplicate samples were taken from each loaded filters. Commercially available HNO$_3$ (70%), H$_2$O$_2$ (30%) and HF (40%) were of ultra pure grade and used for chemical digestion via a high pressure microwave digestion system (Ethos 320; Milestone, Italy). The resulting solutions were heated on a hot plate to evaporate HF and then pure water was added to get solutions for the analysis of trace metals and lead isotope ratios by Inductively Coupled Plasma–Mass Spectrometry (X-7; Thermo-elemental, USA). Indium and iridium with an elemental concentration of 10 ng mL^{-1} were added online by a *Y*-type canal as internal standards for the elemental concentration measurement. The accuracy of the method regarding trace metal determination was evaluated using a standard reference material (SRM 1648, Urban Particulate Matter, National Institute of Standards and Technology, Gaithersburg, MD). The analytical results are presented in Table 1 and they were in good agreement with the certified values, indicating the accuracy of the employed analytical procedures.

For lead isotope ratio measurement, SRM 981 (Common Lead Isotopic Standard, National Institute of Standards and Technology, Gaithersburg, MD) was used for the validation and calibration. The uncertainty levels were about 0.07% for ^{207}Pb/^{206}Pb, 0.09% for ^{208}Pb/^{206}Pb, and 0.3% for ^{206}Pb/^{204}Pb for routine analyses following the literature procedure [7], without any chemical lead purification of the resulting solutions.

3. Results and discussion

3.1. Ambient concentrations of PM$_{2.5}$

The sample-to-sample and site-to-site comparison of the PM$_{2.5}$ mass concentration is statistically presented in Fig. 2. The range of mass concentrations varied significantly over time, from 30 to 143 µg m^{-3} at Baoshan site, from 20 to 124 µg m^{-3} at Putuo site, from 18 to 120 µg m^{-3} at Huangpu site, and from 10 to 67 µg m^{-3} at Jiading site. The annual average concentrations at each location were 84 ± 30, 65 ± 20, 55 ± 18, and

Table 1
Analytical results for urban particulate matter, NIST SRM 1648 (in µg/g)

Element	Certified	Found	Found/certified
As	115 ± 10	116 ± 5	1.00
Cd	75 ± 7	74 ± 3	0.99
Cr	403 ± 12	383 ± 9	0.95
Cu	609 ± 24	597 ± 7	0.98
Fe	39100 ± 1173	36619 ± 984	0.94
Ni	82 ± 3	77 ± 3	0.94
Pb	6550 ± 66	6511 ± 115	0.99
Se	27 ± 1	30 ± 2	1.13
U	5.5 ± 0.1	6 ± 0.1	1.02
V	127 ± 7	130 ± 3	0.93
Zn	4760 ± 143	4864 ± 141	1.02
Ag	6	6 ± 0.1	1.08
Ba	737	706 ± 16	0.96
Bi	No value	7 ± 0.1	–
Ce	55	49 ± 1	0.89
Co	18	17 ± 1	0.97
La	42	35 ± 1	0.84
Mg	8000	6774 ± 116	0.85
Mn	860	776 ± 15	0.90
Sb	45	43 ± 4	0.94
Ti	4000	4121 ± 299	1.03

41 ± 10 µg m^{-3}, respectively. To assess the general pollution levels at the study sites, the present mass concentration data were compared with previously reported data. Ye et al. [11] measured mass concentration in weekly collected PM$_{2.5}$ samples at two residential sites in the same city for a similar 1-year period beginning in March 1999, and the present mass concentrations were in good agreement with their annual average concentration of 60 µg m^{-3}. These values were much higher than the current US EPA recommended annual PM$_{2.5}$ ambient air quality standard [14], which is set at 15 µg m^{-3}. In addition, the lowest value at the control site was 41 ± 10 µg m^{-3} which was roughly close to the 24 h PM$_{2.5}$ US ambient air quality standard of 65 µg m^{-3} [14], indicating that there were significant air pollution levels in Shanghai all through these years.

Overall, the mass concentration at the industrial site of Baoshan was generally the highest among the four sites and it was approximately two times higher than the background level
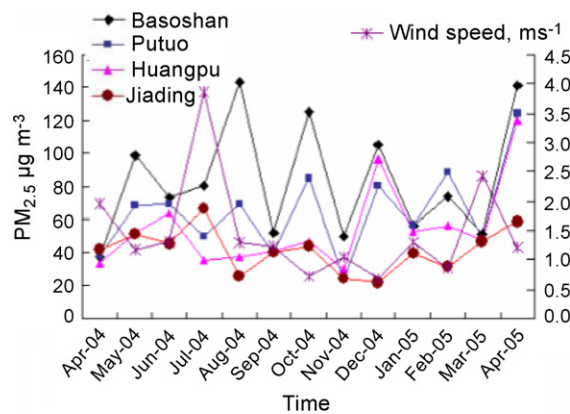

Fig. 2. Sample-to-sample and site-to-site comparison of the PM$_{2.5}$ mass concentration (left *Y*-axes) with associated wind speed (right *Y*-axes) at four sites in Shanghai.

of the control site at Jiading. The higher $PM_{2.5}$ concentrations in site Baoshan, Putuo, Huangpu may reflect a significant contribution of anthropogenic sources compared to the control site. Due to the concurrent sampling done at all four sites with relatively high sampling heights, it could be hypothesized that the influence from occasional pollution episodes on the measurements of $PM_{2.5}$ concentrations was negligible. Since emissions from mobile sources would be ongoing for all urban areas in Shanghai and the daily cycle of mobile emissions would not be expected to have a pronounced variation during the short term of the study, high ambient $PM_{2.5}$ mass concentration peaks occurred only at Baoshan, suggesting that the contribution of stationary industrial emissions was more important than the contribution of mobile sources even in areas with heavy traffic.

Auto-monitoring data of PM_{10} and meteorological parameters for the same sampling period in this work were available at the three SEMC sites. As the ambient $PM_{2.5}$ mass concentration was associated not only with source processes but also with changes in environmental conditions, particularly with wind dynamics, an attempt was made to investigate the direct influence of wind speed on the concentration levels of $PM_{2.5}$ by using a simple evaluation of the spatial variation of $PM_{2.5}$, this is also presented in Fig. 2. Based on wind speed criteria, it was found that the concentrations of $PM_{2.5}$ tended to fall into a relatively narrow range for all four sites when an increase in wind speed occurred. However, under mild wind speeds ($<1.5\,\mathrm{m\,s^{-1}}$), a rough systematic decrease in $PM_{2.5}$ concentrations was seen, beginning from industrial site of Baoshan, followed by Putuo, Huangpu, and then Jiading. This occurred even though the residential and commercial sites of Putuo and Huangpu in the downtown area of Shanghai experienced heavy traffic use. Moreover, a statistical analysis showed there was a moderately linear correlation between the mass concentration at Baoshan and Putuo sites (R^2 of 0.61 and a slope of 0.57). Although much weaker, a positive linear correlation (R^2 of 0.46 and a slope of 0.37) was seen between Baoshan and Huangpu sites. Thus, it seemed that the major source of $PM_{2.5}$ was not the mobile sources, and the influence of localized intense industrial stationary emissions were likely reflecting the regional nature of the high load of $PM_{2.5}$ in Shanghai.

To explore more site-specific information in Shanghai, the $PM_{2.5}/PM_{10}$ ratio and the averaged data of two meteorological parameters are shown in Fig. 3. Relative humidity (RH) and the temperature well elucidated the characteristics of the subtropical and coastal climate of Shanghai. The average values of all samples for the $PM_{2.5}/PM_{10}$ ratio among the three SEMC sites were 0.61 for Baoshan, 0.53 for Putuo, and 0.58 for Huangpu, which appeared to be consistent with reported literature value of 0.59 for urban sites at other locations in China [15]. It has been reported that aerosol samples taken in urban areas showed that mobile source emissions usually constituted the most significant source of $PM_{2.5}$ in urban environments [16]. Since traffic is routinely concentrated in urban areas, the highest ratio of $PM_{2.5}/PM_{10}$ occurred in this work at the industrial site of Baoshan which was in a suburban area further confirming the fact that stationary industrial emissions, other than mobile sources, were the most important contribu-
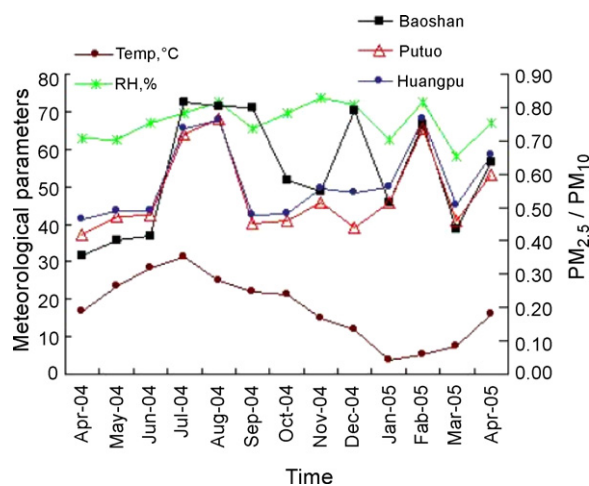

Fig. 3. Averaged auto-monitoring data of meteorological parameters (temperature and relative humidity for left *Y*-axes) and the comparison of calculated $PM_{2.5}$ to PM_{10} ratio at three SEMC sites (right *Y*-axes) during this study.

tor of $PM_{2.5}$ in Shanghai. Thus, it was not surprising to find that the ratios of $PM_{2.5}/PM_{10}$ were not always high in summer and the most notable high ratios in Baoshan sites indicating the significant addition of fine mass concentrations from stationary industrial emissions which were featured as occasional pollution episodes.

3.2. Elemental concentrations in the $PM_{2.5}$ samples

For the assessment of air quality, the concentrations of 21 elements in the $PM_{2.5}$ samples, were analyzed by ICP–MS. Table 2 compares elemental concentrations ($\mathrm{ng\,m^{-3}}$) in $PM_{2.5}$ samples collected at the four study sites. Notably, Cr, Cu, Fe, Ni, Zn, Mg, Mn, and Ti were found at much higher concentrations at Baoshan than at the other three sites. Since the Baoshan industrial zone was the home of the first steel manufacturing enterprise in China, it was suspected that these elements, all found in steels, could be emitted to the atmosphere with the outgoing stack gas during the manufacturing process. This finding was consistent with the levels of $PM_{2.5}$ concentration, suggesting there was the same contribution from localized stationary emission. For more toxic elements, As, Cd, Se, Pb, and Sb, the effect was not that clear as the average concentrations at all four sampling sites were roughly comparable. In general, the lowest concentrations of all detected elements were always found at Jiading. However, in comparison to 10-year average values of airborne PM with diameters less than 2 μm available for Tokyo, another east Asian mega-city which has a similar large population and functions as a commercial and industrial center either [17], it was found that the levels of most of the toxic elements, such as As, Cd, Se, Pb, and Sb, even at their lowest values at the control site of Jiading were much higher than those of Tokyo (1.60, 1.17, 1.30, 39.2, 4.93 $\mathrm{ng\,m^{-3}}$, respectively). The lowest As levels found at Jiading (27 $\mathrm{ng\,m^{-3}}$) were 17 times higher than the Tokyo levels (1.60 $\mathrm{ng\,m^{-3}}$). In summary, the elemental concentrations in air in Shanghai indicated the severe reality of heavy airborne metallic particle pollution.

Table 2
Comparison of elemental concentrations (ng m^{-3}) in daily sampled PM$_{2.5}$ at four sites in Shanghai

Element	Baoshan		Putuo		Huangpu		Jiading	
	Mean	Range	Mean	Range	Mean	Range	Mean	Range
As	32 ± 27	4–92	28 ± 19	4–62	36 ± 28	2–73	27 ± 24	1–67
Cd	4.6 ± 3.2	0.8–12.2	3.7 ± 1.9	1.1–6.4	1.7 ± 1.6	0.2–4.9	1.6 ± 1.0	0.5–4.4
Cr	58 ± 39	5–134	15 ± 10	1–35	19 ± 17	1–70	17 ± 15	3–68
Cu	54 ± 29	10–109	29 ± 19	10–80	33 ± 20	5–72	26 ± 12	7–46
Fe	1187 ± 1193	621–4153	950 ± 520	225–2146	682 ± 488	192–1615	666 ± 202	231–901
Ni	20 ± 14	4–56	8 ± 3	2–13	6 ± 4	2–16	6 ± 5	1–20
Pb	149 ± 122	51–364	143 ± 117	39–460	75 ± 74	15–270	67 ± 51	12–180
Se	4.5 ± 2.8	1.6–9.3	3.1 ± 1.9	0.1–7.0	2.5 ± 2.2	0.6–7.0	1.6 ± 1.3	0.3–4.1
U	0.12 ± 0.06	0.05–0.21	0.17 ± 0.15	0.03–0.56	0.04 ± 0.03	0.01–0.11	0.06 ± 0.03	0.01–0.11
V	17 ± 10	5–34	9 ± 6	2–23	11 ± 10	2–39	4 ± 3	1–11
Zn	681 ± 297	172–1163	349 ± 154	138–641	344 ± 274	92–869	300 ± 183	20–583
Ag	0.27 ± 0.18	0.06–0.78	0.34 ± 0.14	0.07–0.51	0.38 ± 0.36	0.01–1.20	0.18 ± 0.16	0.02–0.55
Ba	15 ± 8	2–33	12 ± 11	1–34	8 ± 6	2–20	10 ± 6	2–21
Bi	1.6 ± 1.3	0.4–4.6	1.3 ± 0.9	0.2–3.2	1.2 ± 1.1	0.1–3.9	0.5 ± 0.4	0.1–1.2
Ce	2.2 ± 0.8	0.9–3.5	1.7 ± 0.9	0.7–4.1	0.8 ± 0.5	0.2–2.1	0.9 ± 0.5	0.2–1.5
Co	1.1 ± 0.5	0.3–2.1	0.8 ± 0.5	0.6–4.4	0.4 ± 0.2	0.1–0.8	0.5 ± 0.3	0.1–1.1
La	1.26 ± 0.48	0.48–1.96	1.02 ± 0.61	0.40–2.65	0.45 ± 0.34	0.06–1.24	0.50 ± 0.28	0.02–1.01
Mg	450 ± 378	58–1316	236 ± 94	69–430	127 ± 119	15–425	139 ± 88	13–338
Mn	113 ± 87	25–328	51 ± 28	17–93	48 ± 41	10–153	29 ± 20	10–87
Sb	33 ± 6	25–45	22 ± 5	13–29	21 ± 5	14–30	22 ± 6	12–35
Ti	61 ± 29	25–117	42 ± 25	1–103	31 ± 16	9–63	32 ± 24	1–64

To get an indication about the extent of the contribution of anthropogenic emissions to atmospheric elemental levels, the results of aerosol-crust enrichment factors (EFs) at the four sites are summarized in Table 3. The EFs were calculated using the following equation:

$$EF_{crust} = \frac{(C_i/C_{Ti})_{PM2.5}}{(C_i/C_{Ti})_{crust}}, \quad (1)$$

where C_i is the concentration of the element considered in the PM$_{2.5}$ or the crust and C_{Ti} is the concentration of reference element (Ti) in the PM$_{2.5}$ or the crust. The elemental concentrations in the crust used in this study were the average data of local Chinese soil composition [18]. This calculation assumed that the anthropogenic contribution of the normalizing element (i.e. Ti) is insignificant. The EFs can be used to identify the potential sources of crustal and anthropogenic components. According to

Table 3
Comparison of enrichment factor (EF) in PM$_{2.5}$ collected at four sites in Shanghai with the data of averaged concentrations in Chinese topsoils used for the calculation

Element	Concentrations in topsoils (μg g^{-1})	Baoshan		Putuo		Huangpu		Jiading	
		Mean	Range	Mean	Range	Mean	Range	Mean	Range
As	9.152	111	91–380	205	168–707	221	208–649	254	154–1267
Cd	0.147	2799	195–24414	2752	354–24186	536	93–1995	739	145–2003
Cr	77.719	25	2–81	8	1–34	11	2–47	12	2–61
Cu	26.255	77	12–147	42	18–89	84	11–296	114	23–199
Fe	38808	2.5	0.9–5.1	1.5	0.4–4.4	1.2	0.3–2.4	1.6	0.3–3.9
Ni	34.123	24	3–66	10	4–34	9	4–19	14	1–39
Pb	25.513	198	81–476	220	72–679	136	36–259	167	24–486
Se	0.119	1281	505–2616	973	76–1507	1061	321–2808	876	102–2395
U	2.603	2	1–3	2	1–6	1	0–2	2	0–6
V	100.721	6	2–14	4	1–9	4	1–9	2	1–7
Zn	77.848	329	66–604	178	108–244	221	68–648	228	26–482
Ag	0.073	139	22–284	213	37–497	289	64–753	186	13–513
Ba	445.374	1.3	0.3–3.0	0.9	0.1–2.5	1.0	0.1–2.4	1.3	0.1–3.9
Bi	0.293	190	62–348	171	41–329	175	61–490	104	20–294
Ce	67.160	1.2	0.5–2.0	1.0	0.5–2.4	0.6	0.2–1.0	1.0	0.2–2.8
Co	15.433	2.8	0.8–5.7	2.2	0.6–4.4	1.2	0.3–1.9	2.4	0.4–6.1
La	34.752	1.4	0.5–2.7	1.2	0.7–3.1	0.6	0.1–1.3	1.0	0.1–3.1
Mg	9594	0.7	0.1–1.4	0.4	0.2–0.9	0.3	0.1–1.4	0.3	0.1–1.2
Mn	708.188	5.8	1.0–19.5	2.8	1.1–5.6	3.1	0.8–5.3	2.1	0.8–4.1
Sb	13.216	2425	857–3936	1335	677–2145	1387	802–2173	1084	616–1670
Ti	4589.878	1	1–1	1	1–1	1	1–1	1	1–1

conventional classification criteria, an EF value lower than 10 is taken as an indication that a trace element in an aerosol has a significant crustal source, while an EF value greater than 10 is considered to indicate a significant proportion of an element with an anthropogenic origin [19].

Among the investigated elements, high EFs values were obtained for As, Cd, Cu, Pb, Se, Zn, Ag, Bi, and Sb (range from 42 to 24, 414 on average), which suggested the predominance of non-crustal sources. Relatively lower EFs values were observed for Cr, Fe, Ni, U, V, Ba, Ce, Co, La, Mg and Mn (range from 0.3 to 25 on average), suggesting a lesser contribution from anthropogenic sources. Compared with the PM_{10} result [4], significant variations of EFs values for this study were calculated for Ag, Ba, and Ni (2.0, 125, and 3.3 for PM_{10}). Since Ba is relatively abundant in the crust and does not belong to volatile element, the low value on average of EF (1.1) in this study indicated this element was not enriched in the fine particles which were more influenced by high temperature combustion and gasification processes, resulting in adsorption of more highly toxic elements such as Ag and Ni. This result was very consistent with the known fact that the coarse fraction particles are composed largely of primary particles with a crustal origin and $PM_{2.5}$ can possibly be representative of combustion-related components which consist of more surface-enriched metal compounds.

In this study, the values of EFs on average showed notable variations for most detected elements from site to site, and the distribution pattern in general of the higher EF values was found to be: Cd > Sb > Se > Zn > As > Pb > Ag > Bi > Cu > Ni > V. Compared with Shanghai's counterpart mega-city of Tokyo again, the variation was Sb > Se > Cd > Pb > Zn > Mo > As > V > Cu > Ni and there was a great difference associated with the sequence of Sb and V (20 900 and 473) [17]. It has been demonstrated that a significant source of Sb is from brake pad wear of automobiles and V is known to be released from combustion of fossil fuel, particularly in diesel engines, and the more serious pollution levels of Sb and V exhibited a more significant contribution from vehicle emissions to airborne fine particles in Tokyo than in Shanghai. Thus, it appeared that there was another important air pollution source other than traffic-derived emissions in Shanghai. Undoubtedly, it became apparent that these metal concentrations in $PM_{2.5}$ in Shanghai related to none-mobile source fuel combustion are more important. It was worth noting that the airborne Sb concentration is much higher than that of As in Tokyo [17], while a slightly higher As concentration than that of Sb was observed in $PM_{2.5}$ in Shanghai. The fact should be pointed out that the economic, industrial, and demographic characteristics of Shanghai are quite different from those of Japan, North America and Europe [5,6,20–22]. In China, air pollution is mostly associated with huge and low-efficiency energy consumption and energy mainly comes from coal-fired power stations (near 80%) [23]. Coal analyses have indicated that certain elements (Pb, Hg, As, Cu, Zn, Cd, Se, Sn, Ba, Ce, Cs, Mn, etc.) are ubiquitous in the matrix, and experiments have indeed demonstrated [24,25] that coal trace elements, particularly the volatile element, such as Hg, and semivolatile

elements, such as As, Cd, Cu, Pb, Se, and Zn, are released to the atmosphere in effluents of most combustion processes. In Shanghai the total coal consumption has increased from year to year, and the amount of coal consumption was about 51.44 million tons in 2004 [26]. It has been reported that Chinese coal, especially, northern Chinese coal contains a high concentration of As (>100 mg kg^{-1}) [27]. Concerning the resulting emission of volatile metallic species from coal use and the much higher concentrations of semivolatile elements in the air in Shanghai, the comparison of chemical composition of airborne fine particles between Shanghai and Tokyo confirmed the primary contribution of the stationary industrial sources, rather than mobile traffic emissions, to $PM_{2.5}$ concentration levels in Shanghai. Understanding the sources of metal pollution required a good emission inventory, which is not currently available. However, considering the fact that the concentration ratio of Sb to As in the earth's crust is 1/10 [28], the similarly high concentrations of As and Sb observed in $PM_{2.5}$ in Shanghai may suggest a significant emission of Sb from car brake wear. It needs further work to investigate the differences in As and Sb from studies in Japan and China.

3.3. Lead isotopic compositions of $PM_{2.5}$ samples

The isotopic compositions of lead in $PM_{2.5}$ samples collected at the four sites are presented in Fig. 4. The data for source-related samples showed in this figure are cited from literature [7]. In order to observe the contribution from the decay of Th, $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$ ratios are used as Y and X-axes, respectively. Moreover, this permits an easy comparison to recent results because measurements of these two ratios are more precise. The lead growth curve in Fig. 4 was from Cumming and Richard [29]. Since Pb isotope ratio depends on the geological source, the geochemical characteristics of Th-rich environment in China result in the relatively high ^{208}Pb abundance of Chinese-sourced lead which did not fall along the growth curve.

As can be seen in Fig. 4, the site-to site variation of $PM_{2.5}$ samples was found to have little difference, although several
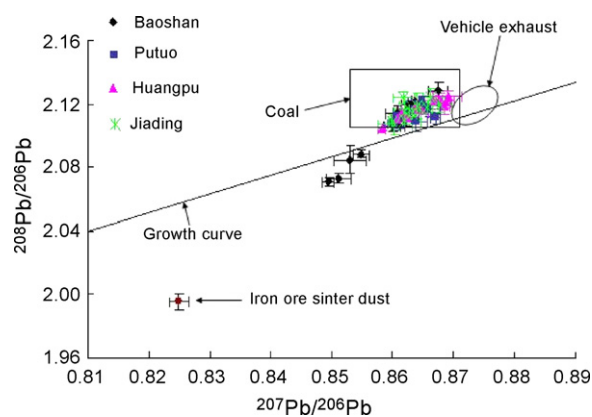

Fig. 4. Stable lead isotopic composition in $PM_{2.5}$ samples and in some source-related samples. The error bar shown is ±1 standard deviation. The data for source-related samples showed in this figure are cited from literature [7].

samples of PM$_{2.5}$ collected at industrial site of Baoshan fell off the line. There are no notable metal mines around Shanghai, and the major iron ore is mostly imported from Australia with a very low value of 0.744 for ^{207}Pb/^{206}Pb, or the raw materials may come from metal reuse [7]. The distinctly downward shift of the exceptional isotopic ratio of PM$_{2.5}$ samples at Baoshan clearly showed the inherited association to iron ore dust from emissions resulting from manufacturing activities and indicating industrial pollution episodes. When compared to the standard lead growth curve of Cumming and Richard, the lead isotope ratio of most PM$_{2.5}$ samples did not fall along the growth curve and showed upward shift, conforming the domestic source of atmospheric lead. Moreover, the lead isotope ratios in PM$_{2.5}$ at the control site, Jiading, which were approximately the same as those of the urban sites of Putuo and Huangpu, implied that ambient background pollutants at different sites were strongly influenced by a more general anthropogenic factor through the long-range transport rather than a localized factor. The similarity of lead isotope ratio in PM$_{2.5}$ over an enlarged area suggested that the air pollution caused by fine particles was developing into a regional problem and the different emission source contributions to PM$_{2.5}$ in Shanghai were strongly affected by a more general set of apportionment at all sampling locations.

As also can be seen in Fig. 4, the current lead isotopic compositions of samples with an origin dominated as gasoline end-member were located outside the line for PM$_{2.5}$ samples, indicating that lead in PM$_{2.5}$ in Shanghai was rarely from mobile fossil fuel combustion. This would be clearly consistent with the policy change of completely banning of leaded gasoline since 1997. As the most important industrial and commercial sector of China, Shanghai has been faced with serious problems of air quality due to increased energy consumption and vehicle quantity. Much has been done about coal combustion in China and the associated sulphur dioxide emissions [6,23,30]. It has been pointed out that the atmospheric SO$_2$ burden from coal burning represented a significant health risk in east China [12,23]. Moreover, attention should be paid to the fact that the large quantities of coal being used to fuel a fast-growing industrial economy were not only responsible for the atmospheric SO$_2$ burden but also caused the higher Pb burden in the air. In this study, the lead isotope ratios of PM$_{2.5}$ were 0.863 ± 0.03 for ^{207}Pb/^{206}Pb and 2.113 ± 0.009 for ^{208}Pb/^{206}Pb which both fell well within the scope of coal Pb isotopic composition (0.860 ± 0.010 for ^{207}Pb/^{206}Pb and 2.121 ± 0.018 for ^{208}Pb/^{206}Pb) [7]. Thus, the former conclusion based on the calculation of isotope ratio and chemical mass balance of the PM$_{10}$ samples that had revealed that coal combustion dominated the lead pollution after the phasing-out of leaded gasoline in 1997 [8], was consistently validated in the present study. Stationary industrial emissions were continuously homogenized and served as the dominant constant-supply reservoir to PM$_{2.5}$ in Shanghai.

Acknowledgements

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