

## Lead concentrations in fine particulate matter after the phasing out of leaded gasoline in Xi'an, China

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### ABSTRACT

Daily concentrations of lead (Pb) were determined for PM<sub>2.5</sub> samples collected from an urban location in Xi'an, China from 2007 to 2009 to assess the effects of the phasing out of leaded gasoline in 2000. The Pb concentrations (annual average: 0.306 μg m<sup>-3</sup>, range: below detection limit to 2.631 μg m<sup>-3</sup>) have declined after the phasing out of leaded gasoline, but the concentrations were still higher than those reported in many other cities. Seasonal variations of Pb were significant, with high concentrations in winter, presumably due to the burning of coal, and low concentrations in summer, due to a deep mixed layer and scavenging of aerosols by precipitation. Correlation analyses and enrichment factor calculations both indicated that anthropogenic sources had a large influence on atmospheric Pb. The lead isotope ratios were low in winter (the average <sup>207</sup>Pb/<sup>206</sup>Pb ratio was 0.843 ± 0.032; <sup>208</sup>Pb/<sup>206</sup>Pb was 1.908 ± 0.058) and high in summer (<sup>207</sup>Pb/<sup>206</sup>Pb was 0.860 ± 0.032; <sup>208</sup>Pb/<sup>206</sup>Pb was 2.039 ± 0.057), suggesting that coal combustion was the major Pb source in winter and vehicular emission was the major Pb source in summer. Positive Matrix Factorization receptor model indicated that there were five major sources for Pb in PM<sub>2.5</sub>. Coal combustion was the major contributor, accounting for 39.0% PM<sub>2.5</sub> mass, followed by vehicular emissions (30.4%). Other contributors included 17.8% from industrial emissions, 11.6% from biomass burning, and 1.2% from fugitive dust.

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### 1. Introduction

Industrialization, urbanization, and rapid economic growth in China have increased the country's demand for energy, and this has led to a profound deterioration of urban air quality. Much of the fine particulate matter (PM<sub>2.5</sub>, particulate matter (PM) with aerodynamic diameters ≤ 2.5 μm) in the atmosphere is produced by anthropogenic activities. This is an especially important component of the atmospheric aerosol because it adversely affects human health, having been linked to respiratory diseases and increased mortality (Lee et al., 2006). Fine PM can penetrate deeply into the lungs (Owen and Ensor, 1992; Seaton et al., 1995), and the toxicity of the fine PM is higher than that of coarser particles (Pacyna, 1995). In

addition, anthropogenic fine particles are often enriched with toxic heavy metals, which are of particular concern for human health (Dockery and Pope, 1996).

Lead (Pb), a cumulative heavy metal toxicant, enters the human body via the inhalation of Pb-bearing particles and by the ingestion of food and water contaminated with Pb (Wang and Zhang, 2006). Even small amounts of Pb can be harmful, particularly to the nervous and hematopoietic systems, and it can impair growth and mental function (Wang and Zhang, 2006). Due to these adverse effects, blood Pb levels in adults and children have been assessed in many human exposure assessment studies (Fawcett et al., 1996). On a global basis, anthropogenic inputs of Pb greatly exceed those from natural sources, accounting for 96% of the total emissions (Nriagu, 1989). Moreover, Pb is the only metal listed in ambient air quality standards in China. The annual maximum acceptable limits for Pb in total suspended particles (TSP, PM with aerodynamic diameters ≤ 100 μm) are 1.0 μg m<sup>-3</sup> and 0.5 μg m<sup>-3</sup>, for China and Europe, respectively; lower than the three-month running average of TSP

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Pb of  $1.5 \mu\text{g m}^{-3}$  in U.S. Therefore, controlling Pb pollution to an acceptable level is important in both environmental health and economic terms.

Xi'an (E  $108^{\circ}09'$  N  $34^{\circ}02'$ ), the capital of Shaanxi Province, is a large industrial city in northern China, situated in the middle of the Yellow River valley and the center of the Central Shaanxi Plain. Xi'an occupies an area of about  $9983 \text{ km}^2$ , with a population of approximately 8 million. The average temperature, precipitation, and relative humidity in Xi'an were  $15.2^{\circ}\text{C}$ ,  $628.0 \text{ mm}$ , and  $61.9\%$  during 2007–2009, respectively (China Statistical Yearbook, 2008, 2009, 2010). Airborne PM is a major air pollution problem throughout much of northwestern China, and Xi'an is subjected to high concentrations of atmospheric particulate matter for much of the year (Cao et al., 2005; Li and Feng, 2010; Shen et al., 2009).

The annual average TSP Pb concentration in Xi'an four sampling sites was  $1.470 \mu\text{g m}^{-3}$  from September 1996 to August 1997 (Zhang et al., 2002), and exceeds China air quality standard for Pb of  $1.0 \mu\text{g m}^{-3}$ . During the periods of 1970s and 1980s, most of the ambient Pb contaminant was attributed to the use of leaded gasoline, and the emissions of Pb from automobiles were estimated to exceed the emissions from pollution point sources (Kabata-Pendias and Mukherjee, 2007). In the 1990s, strict regional regulations eliminated the use of leaded gasoline in developed countries (Kabata-Pendias and Mukherjee, 2007), and the use of leaded gasoline in Xi'an was banned after 2000. Before the phasing out of leaded gasoline in China, the average Pb content in gasoline was  $0.70 \text{ g L}^{-1}$  (Faiz et al., 1996); compared to  $0.005 \text{ g L}^{-1}$  after phasing out of leaded gasoline (China's gasoline specification, "GB17930-1999: Unleaded Gasoline for Motor Vehicles"; Yang and Wang, 1999, and the newest gasoline specification, "GB17930-2006: Gasoline for Motor Vehicles"; Ni et al., 2006). Moreover, the number of motor vehicles has increased by fourfold from 2000 (261,960 vehicles; Chen, 2001) to 2009 (1,012,937 vehicles; Li and Li, 2010) in Xi'an.

The objectives of the present study were to: (1) determine  $\text{PM}_{2.5}$  Pb concentrations in Xi'an following the phase-out of leaded gasoline, (2) evaluate seasonal patterns in the  $\text{PM}_{2.5}$  Pb concentrations, and (3) apportion the sources of  $\text{PM}_{2.5}$  Pb by using enrichment factors, correlation analyses, lead isotope ratios, and Positive Matrix Factorization (PMF) receptor model. This information will be useful for evaluating the effectiveness of pollution controls and air quality management policies.

## 2. Materials and methods

### 2.1. Sample collection

The sampling site was in the southeastern part of downtown Xi'an in a mixture of urban/industrial/commercial/vehicular area (Fig. S1). The samplers were deployed approximately 10 m above ground level, on the roof of a two-story building housing the Institute of Earth Environment, Chinese Academy of Sciences. Daily  $\text{PM}_{2.5}$  samples were collected from 1 January 2007 to 31 December 2009 and every-third-day  $\text{PM}_{10}$  (PM with aerodynamic diameters  $\leq 10 \mu\text{m}$ ) samples were collected in 2007. Twenty-four hour (from 10:00 a.m. to 10:00 a.m. local time of next day) samples were collected using the mini-volume air samplers (Airmetrics, Eugene, OR, USA) that operated at a flow rate of  $5 \text{ L min}^{-1}$ . For isotope Pb analysis, 24-h (from 10:00 a.m. to 10:00 a.m. local time of next day)  $\text{PM}_{2.5}$  samples were also collected every sixth day using a TE-6001 high-volume  $\text{PM}_{2.5}$  sampler (Tisch Environmental Inc. Ohio, USA) with a flow rate of  $1000 \text{ L min}^{-1}$  in July and December 2008, January, February, and July 2009. A total of 1073 and 20 mini-volume and high-volume  $\text{PM}_{2.5}$  samples, respectively, and 112  $\text{PM}_{10}$  samples were collected using pre-fired ( $780^{\circ}\text{C}$ , 3 h) 47 mm

Whatman quartz-fibre filters (QM/A<sup>®</sup>, Whatman Inc., U.K.). Collocated samplings on Teflon<sup>®</sup>-membrane filters were conducted from 9th to 29th October 2009 for Pb comparison.

### 2.2. Mass analysis

For mass determinations, the filters were weighed before and after sampling, allowing at least 24 h for equilibration at a temperature ( $20\text{--}23^{\circ}\text{C}$ ) and relative humidity ( $35\text{--}45\%$ ) controlled environment. Mass concentrations were determined with a Sartorius ME 5-F electronic microbalance that has a sensitivity of  $\pm 1 \mu\text{g}$  (Sartorius, Gottingen, Germany). After weighing, the particle laden quartz-fiber filters were placed in clean plastic bags and refrigerated at  $<4^{\circ}\text{C}$  to minimize the evaporation of volatile components prior to chemical analysis; approximate 10% of the samples are submitted for replicate analysis, the allowable absolute errors between duplicate weights were set to  $\leq 0.015 \text{ mg}$  for blank filters and  $\leq 0.020 \text{ mg}$  for filter samples.

### 2.3. Carbonaceous aerosol analysis

Organic carbon (OC) and elemental carbon (EC) concentrations along with its eight thermal carbon fractions were determined for  $0.526 \text{ cm}^2$  aliquots punched out of the  $\text{PM}_{2.5}$  quartz-fibre filter samples. A Desert Research Institute (DRI) Model 2001 Thermal/Optical Carbon Analyzer (Atmoslytic Inc., Calabasas, CA, USA) was used for carbon analysis following the IMPROVE\_A (Interagency Monitoring of Protected Visual Environment) thermal/optical reflectance protocol (Chow et al., 1993, 2001, 2004, 2005, 2007). Detailed information on carbon analysis and required quality assurance and quality control are documented in Chow et al. (2011).

### 2.4. Elemental analysis

Energy Dispersive X-Ray Fluorescence (ED-XRF) spectrometry (Epsilon 5 ED-XRF, PANalytical B. V., the Netherlands) was used to determine the concentrations of the elements collected on the  $\text{PM}_{2.5}$  quartz-fibre filters (Steinhoff et al., 2000; Wasson and Guo, 2002). Using a three-dimensional polarizing geometry with eleven secondary targets (i.e.,  $\text{CeO}_2$ , CsI, Ag, Mo, Zr, KBr, Ge, Zn, Fe, Ti, and Al) and one barkla target ( $\text{Al}_2\text{O}_3$ ), good signal to background ratio and low detection limits were achieved. The X-ray source is a side window X-ray tube with a gadolinium anode, operated at an accelerating voltage of  $25\text{--}100 \text{ kV}$  and a current of  $0.5\text{--}24 \text{ mA}$  (maximum power:  $600 \text{ W}$ ). The characteristic X-ray radiation is detected by a germanium detector (PAN 32). Each sample was analyzed for 30 min to obtain a spectrum of X-ray counts versus photon energy, with the individual peak energies matching specific elements, and peak areas corresponding to elemental concentrations (Brouwer, 2003). The ED-XRF spectrometer was calibrated with thin-film standards obtained from MicroMatter Co. (Arlington, WA, USA). In total, 15 elements (i.e., S, Cl, K, Ca, Ti, Cr, Mn, Fe, Ni, Zn, As, Br, Mo, Cd, and Pb) were determined.

### 2.5. Pb isotopic compositions analysis by ICP-MS

The analysis of Pb isotopic compositions, including  $^{204}\text{Pb}$ ,  $^{206}\text{Pb}$ ,  $^{207}\text{Pb}$ , and  $^{208}\text{Pb}$ , were conducted using a Thermo Elemental X Series ICP-MS equipped with a high performance sample interface (Thermo Fisher Scientific, USA). Each filter was digested in  $4 \text{ ml } 1:1 \text{ (V:V)}$  nitric acid and American Society for Testing Material (ASTM) Type 1 water at  $95^{\circ}\text{C}$  for 45 min. The samples were brought to a final volume of  $50 \text{ ml}$ , resulting in a final acid concentration of 4%. An Environmental Express Hot Block enclosed in a HEPA filtered enclosure was used for the digestion. The Pb isotopic ratios of  $^{207}\text{Pb}/^{206}\text{Pb}$  and  $^{208}\text{Pb}/^{206}\text{Pb}$

were calculated from the average of 7 runs consisting of 100 mass sweeps, with a sampling time of 50 ms per mass. The data were corrected to the NIST SRM 981 Pb isotope standard.

### 2.6. Accuracy and precision of $PM_{2.5}$ Pb by ED-XRF

Based on the 19 sets of collocated measurement using quartz-fibre and Teflon<sup>®</sup>-membrane filters, Fig. S2 of the supplementary data shows high correlation ( $R = 0.97$ ,  $P < 0.0001$ ) with a slope of 1.10 and low intercept ( $0.06 \mu\text{g m}^{-3}$ ). Experimental results showed that the ED-XRF analysis of the quartz-fibre filters can meet the quality assurance objectives for many heavy elements including Pb. Moreover, National Institute of Standards and Technology (NIST) Standard Reference Material<sup>®</sup> (SRM) 2783 was employed to validate the accuracy of the instrument. The reference value for Pb in SRM 2783 is  $317 \pm 54 \mu\text{g}/\text{filter}$  by using the ED-XRF method, which was similar to the results analyzed by our ED-XRF (the eleven times average concentration of Pb was  $319 \pm 88 \mu\text{g}/\text{filter}$ ). The relative error was approximately 0.6%, which is well within the required range of error, demonstrating the accuracy of Pb concentrations analyzed by ED-XRF. Replicate Pb analysis of one quartz-fibre filter sample (five times) yielded an analytical precision of 7.9%; and replicate analysis were conducted on every 8th sample. Laboratory blanks of the quartz-fibre filters were analyzed to derive a minimum detection limit (MDL) of  $21 \text{ ng m}^{-3}$  for Pb.

### 2.7. Enrichment factors (EFs)

Atmospheric concentrations of trace metals often vary by orders of magnitude, but by normalizing the concentrations relative to the values expected from known or expected sources, one can gain some insight into the chemical character of aerosols (Chester et al., 1993; Rahn, 1976). Enrichment factors (EFs) calculated relative to a reference for the earth's upper continental crust (Taylor and McLennan, 1986) have been used to evaluate crustal versus non-crustal contributions to elemental aerosol loadings. The detailed method, formula, and evaluation criterion have been described in Zhuang et al. (2001).

### 2.8. Positive matrix factorization (PMF) analysis

Receptor model by Positive Matrix Factorization (PMF 3.0, developed by the U.S. Environmental Protection Agency) provides ways of apportioning the measured ambient  $PM_{2.5}$  Pb concentrations to potential pollutant sources. This model is a multivariate factor analysis technique that decomposes chemical sample data into two matrices: factor contributions and factor profiles (Paatero and Tapper, 1993, 1994; Paatero, 1997). Because PMF is a descriptive model, the choice of factors retained is subjective since there are no objective criteria for choosing ideal solutions. Too few factors may combine multiple sources whereas too many factors can split one bona fide factor into two or more erroneous or un-interpretable sources. This method was detailed by Paatero and Tapper (1993, 1994). In this study, the final PMF solution was determined by choosing the most stable results with respect to different input options and choosing the one with the most physically interpretable profiles.

## 3. Results and discussion

### 3.1. $PM_{2.5}$ Pb concentrations in Xi'an

The  $PM_{2.5}$  Pb concentrations from 2007 to 2009 in Xi'an ranged from  $<0.021$  (i.e., MDL for Pb) to  $2.631 \mu\text{g m}^{-3}$  (on January 21, 2007), and the average value ( $0.306 \pm 0.274 \mu\text{g m}^{-3}$ ) was well below China

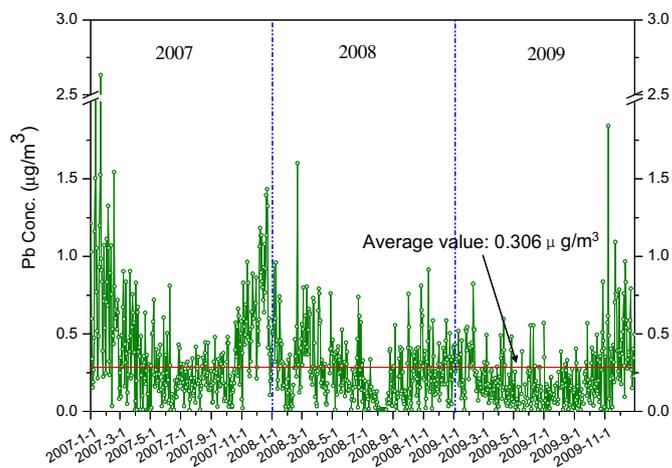


Fig. 1. Time series of daily  $PM_{2.5}$  Pb concentrations from Xi'an, China.

air quality standard of  $1.0 \mu\text{g m}^{-3}$  for TSP Pb, with only two days exceeding the standard during 2007–2009. Past studies (listed in Table S1 of the supplementary data) showed that Pb concentrations in Xi'an ranked the highest with the exception of Agra, India (Kulshrestha et al., 2009). For instance,  $PM_{2.5}$  Pb concentrations from Beijing ranged from  $0.037$  to  $0.207 \mu\text{g m}^{-3}$  in summer and from  $0.045$  to  $1.447 \mu\text{g m}^{-3}$  in winter (2002), with an average concentrations of  $0.110 \mu\text{g m}^{-3}$  and  $0.311 \mu\text{g m}^{-3}$  for summer and winter, respectively (Sun et al., 2006). These averages are 60.7 and 30.9% lower than those in Xi'an (average concentrations were  $0.280 \mu\text{g m}^{-3}$  in summer and  $0.450 \mu\text{g m}^{-3}$  in winter). The Pb concentrations in Shanghai (Ye et al., 2003) were  $0.080$ – $0.590 \mu\text{g m}^{-3}$  from 1999 to 2000, with an average of  $0.280 \mu\text{g m}^{-3}$ , which was 8.5% lower than the average value of Pb in Xi'an. Pb concentrations in several U.S. cities (Gao et al., 2002) ranging from  $0.005$  to  $0.008 \mu\text{g m}^{-3}$  (1998–2000) were distinctly lower than those in Xi'an;  $PM_{2.5}$  Pb in European cities (e.g., Sweden, Greece, and Spain) were also low in the range of  $0.06$ – $1.43 \mu\text{g m}^{-3}$  (Boman et al., 2009; Thomaidis et al., 2003; Querol et al., 2001).

As vehicles equipped with catalytic converters are gradually penetrated to the motor vehicle fleet, ambient  $PM_{2.5}$  Pb concentrations in Xi'an declined from  $0.418 \mu\text{g m}^{-3}$  in 2007, to

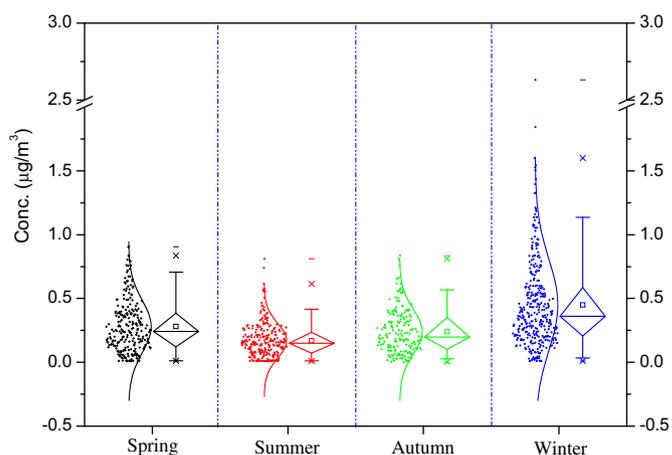


Fig. 2. Seasonal variations of  $PM_{2.5}$  Pb concentrations in Xi'an from 2007 to 2009 [The box plots indicate the seasonal average concentration and the min, 1st, 25th, 50th, 75th, 99th, and max percentiles. A normal curve is fitted to the measurements. (spring: March–May; summer: June–August; autumn: September–October, and winter: November–February)].

**Table 1**  
Enrichment factors of various elements in PM<sub>2.5</sub> from Xi'an (using Fe as the normalizing element).

Element	Concentration (μg/m <sup>3</sup> )	Crustal Abundance <sup>a</sup>	Enrichment Factor (EF)
Pb	0.306	20 × 10 <sup>-6</sup>	405
As	0.027	1.5 × 10 <sup>-6</sup>	476
Zn	1.607	71 × 10 <sup>-6</sup>	599
Fe	1.323	3.5%	1
K	1.573	2.8%	1
Ca	1.611	3.0%	1
Ti	0.116	3000 × 10 <sup>-6</sup>	1
Cr	0.014	355 × 10 <sup>-6</sup>	1
Mn	0.105	600 × 10 <sup>-6</sup>	5
Ni	0.007	20 × 10 <sup>-6</sup>	9

<sup>a</sup> Taylor and McLennan, 1986.

0.264 μg m<sup>-3</sup> in 2008, and 0.237 μg m<sup>-3</sup> in 2009. Zhang et al. (2002) showed that the annual average TSP Pb concentration in 1997 (1.470 μg m<sup>-3</sup>) was 2.5–3.5 times higher than those of PM<sub>10</sub> and PM<sub>2.5</sub> Pb concentrations (0.535 μg m<sup>-3</sup> and 0.418 μg m<sup>-3</sup>, respectively) in 2007 in Xi'an. Nonetheless, a comparison with a previous study conducted in Xi'an showed that the three year average (2007–2009) PM<sub>2.5</sub> Pb concentration during autumn and winter (0.345 μg m<sup>-3</sup>) was 46.1% lower than that from 2003 to 2004 (0.640 μg m<sup>-3</sup>, Li, 2004).

The PM<sub>2.5</sub> Pb accounted for 67.0–82.8% of the PM<sub>10</sub> Pb in 2007, consistent with other studies (Li et al., 2009a; Sun et al., 2006), which have shown that Pb was more abundant in fine than coarse fraction of PM. This is significant from a public health standpoint because fine PM can penetrate more deeply into the respiratory system than coarse particles. In addition, fine particles can be transported over long distances because of their relatively long residence time in the atmosphere.

### 3.2. Temporal variations of atmospheric Pb in Xi'an

Fig. 1 exhibited daily variations of PM<sub>2.5</sub> Pb concentrations, especially during winter time with the concentrations varied by over two orders of magnitude from 0.009 to 2.631 μg m<sup>-3</sup> (average of 0.450 μg m<sup>-3</sup>). Less variations were observed in other seasons. Similar temporal pattern was found from year to year.

Seasonal variations in Fig. 2 showed that winter PM<sub>2.5</sub> Pb concentrations were about 2.5 times of those in summer, with the similar levels during spring and autumn. The observed seasonality

was consistent with those of Beijing (Sun et al., 2006) and Tianjin (Wang et al., 2006). During the heating season (November 15 to March 15), elevated PM<sub>2.5</sub> Pb concentrations may be attributed to the increased residential coal burning and a stable atmospheric boundary layer with a shallow mixing layer depth (for example, average temperature of 5.6 °C and wind speed of 7 km h<sup>-1</sup> in 2007 winter, China Statistical Yearbook, 2008). High temperature with increased precipitation and high wind speed (for example, 25.9 °C, 10 km/h, and 479.7 mm, respectively, in 2007 summer, China Statistical Yearbook, 2008) in summer favored atmospheric convection and dispersion that led to lower summer concentrations.

Similar seasonal pattern was found for PM<sub>2.5</sub> Pb/mass ratios in 2007 ranging from 0.26% in winter to 0.15% in summer (Fig. S3A). PM<sub>coarse</sub> (PM<sub>10</sub> - PM<sub>2.5</sub>) Pb in 2007 also varied by fivefold between seasons (Fig. S3B), with the highest concentration found in winter (0.275 μg m<sup>-3</sup>) and the lowest in autumn (0.054 μg m<sup>-3</sup>). Primary PM emitted during coal combustion typically has a bimodal distribution: a submicrometer mode (~0.1 μm) and a large particle mode (between 1 and 10 μm) (Kaupplinen and Pakkanen, 1990; McElroy et al., 1982; Taylor and Flagan, 1982; Quann et al., 1982). Therefore, elevated PM<sub>coarse</sub> Pb during winter was mainly also attributed to coal burning, since there is no other Pb sources in the area. Elevated PM<sub>coarse</sub> Pb during spring (0.175 μg m<sup>-3</sup>) was attributed to the Asian dust storms, while large quantities of coarse particles (with significant amounts of metal elements) are transported over north China (Zhang et al., 2005; Zhuang et al., 2001).

### 3.3. Sources for Pb in PM<sub>2.5</sub> from Xi'an

#### 3.3.1. Enrichment factors (EFs)

Table 1 showed the enrichment factors (EFs, normalized to Fe) for Pb, Zn, and As ranged from 405 to 599, suggesting an anthropogenic sources origin. The EFs for K, Ca, Ti, Cr, and Mn were equal to or lower than 5, demonstrating that these elements are mainly from natural crustal sources. The EF for Ni was 9, which indicated that this element has both natural and anthropogenic sources. The largest natural sources for Ni are volcanoes and the weathering of the continental crust, but Ni has been perturbed to a degree by anthropogenic activities, especially fossil fuel combustion (Nriagu, 1989). The EFs for Pb decreased with time, with values of 553, 349, and 313 for 2007, 2008 and 2009, respectively, consistent with removing Pb as additive in gasoline.

**Table 2**  
Pb isotopic compositions in PM<sub>2.5</sub> for source and ambient samples acquired in this study.

Material and location	<sup>207</sup> Pb/ <sup>206</sup> Pb		<sup>208</sup> Pb/ <sup>206</sup> Pb		Reference
	Average	Range	Average	Range	
Ambient samples (summer in Xi'an)	0.860 ± 0.032 <sup>a</sup>	0.841–0.887	2.039 ± 0.057 <sup>a</sup>	1.902–2.223	This study
Ambient samples (winter in Xi'an)	0.843 ± 0.032 <sup>a</sup>	0.781–0.873	1.908 ± 0.058 <sup>a</sup>	1.623–2.054	
<i>Vehicle exhaust samples</i>					
Shanghai	0.885	0.878–0.893	2.145	2.139–2.151	Zheng et al. (2004)
Shanghai (leaded gasoline)	0.901	0.896–0.911	2.194	2.187–2.201	Chen et al. (2005)
Shanghai (unleaded gasoline)	0.872	0.862–0.879	2.124	2.118–2.130	
Beijing	0.866				Mukai et al. (1993)
Hong Kong	0.862		2.089		Lee et al. (2007)
Pearl River Delta	0.862		2.085		Zhu et al. (2001)
<i>Coal combustion samples</i>					
Chinese northern coal	0.847	0.84–0.86			Mukai et al. (2001)
Coal used in Beijing	0.849				Mukai et al. (1993)
Coal used in Shanghai		0.846–0.867			Zheng et al. (2004)
Coal used in Shanghai	0.860	0.828–0.877			Chen et al. (2005)
Coal combustion dust in Shanghai	0.857	0.853–0.860			
Coal fly ash in Shanghai	0.858	0.855–0.861			

<sup>a</sup> Uncertainty.

### 3.3.2. Correlations between Pb and other aerosol constituents

Fig. S4 of the supplementary data showed the highest correlation between  $PM_{2.5}$  Pb and As ( $R = 0.91$ ,  $P < 0.0001$ ), consistent with coal combustion emission. For each ton of permo-carboniferous coal (containing roughly  $5 \text{ mg kg}^{-1}$  As) burned, power stations emit roughly 0.40 g As into the atmosphere, most of which is associated with fly ash (Luo et al., 2004). Although coal combustion is one of the major sources for As in the atmosphere (Xie et al., 2006), lesser amounts of As also originate from vehicular emissions and oil combustion (Freitas et al., 2004; Thomaidis et al., 2003). A moderate correlation ( $R = 0.73$ ,  $P < 0.0001$ , Fig. S4B) between Pb and OC2 (organic carbon evolved at  $280^\circ\text{C}$  in He atmosphere) also supported the notion of coal combustion (Cao et al., 2005). Moderate correlations were also observed between Pb and EC1 (low temperature elemental carbon evolved at  $580^\circ\text{C}$  in 2%  $\text{O}_2/98\%$  He atmosphere,  $R = 0.73$ ), and EC ( $R = 0.80$ ), markers of motor vehicle emissions (Bennet

et al., 2005; Cao et al., 2005; Kulshrestha et al., 2009; Wang et al., 2008).

### 3.3.3. Characteristics of Pb isotope compositions

Lead has four naturally occurring stable isotopes,  $^{204}\text{Pb}$ ,  $^{206}\text{Pb}$ ,  $^{207}\text{Pb}$ , and  $^{208}\text{Pb}$ . The last three Pb isotopes are radiogenic, and are the end-products of  $^{238}\text{U}$ ,  $^{235}\text{U}$ , and  $^{232}\text{Th}$ , respectively (Dickin, 1995). Because the isotopic composition of Pb from each source is different, the Pb isotopic ratios can provide complementary information on the source of Pb and it can be a reliable tool for identifying anthropogenic source. Twenty high-volume  $PM_{2.5}$  samples representing the period of summer (July 2008 and July 2009; 10 samples) and winter (December 2008 and January, February 2009; 10 samples) were selected for measuring Pb isotopic compositions. As shown in Table 2, isotope ratios ranged from 0.781 to 0.887 for  $^{207}\text{Pb}/^{206}\text{Pb}$  and from 1.623 to 2.223 for  $^{208}\text{Pb}/^{206}\text{Pb}$ . The seasonal variations of isotope ratios were pronounced, being low in winter

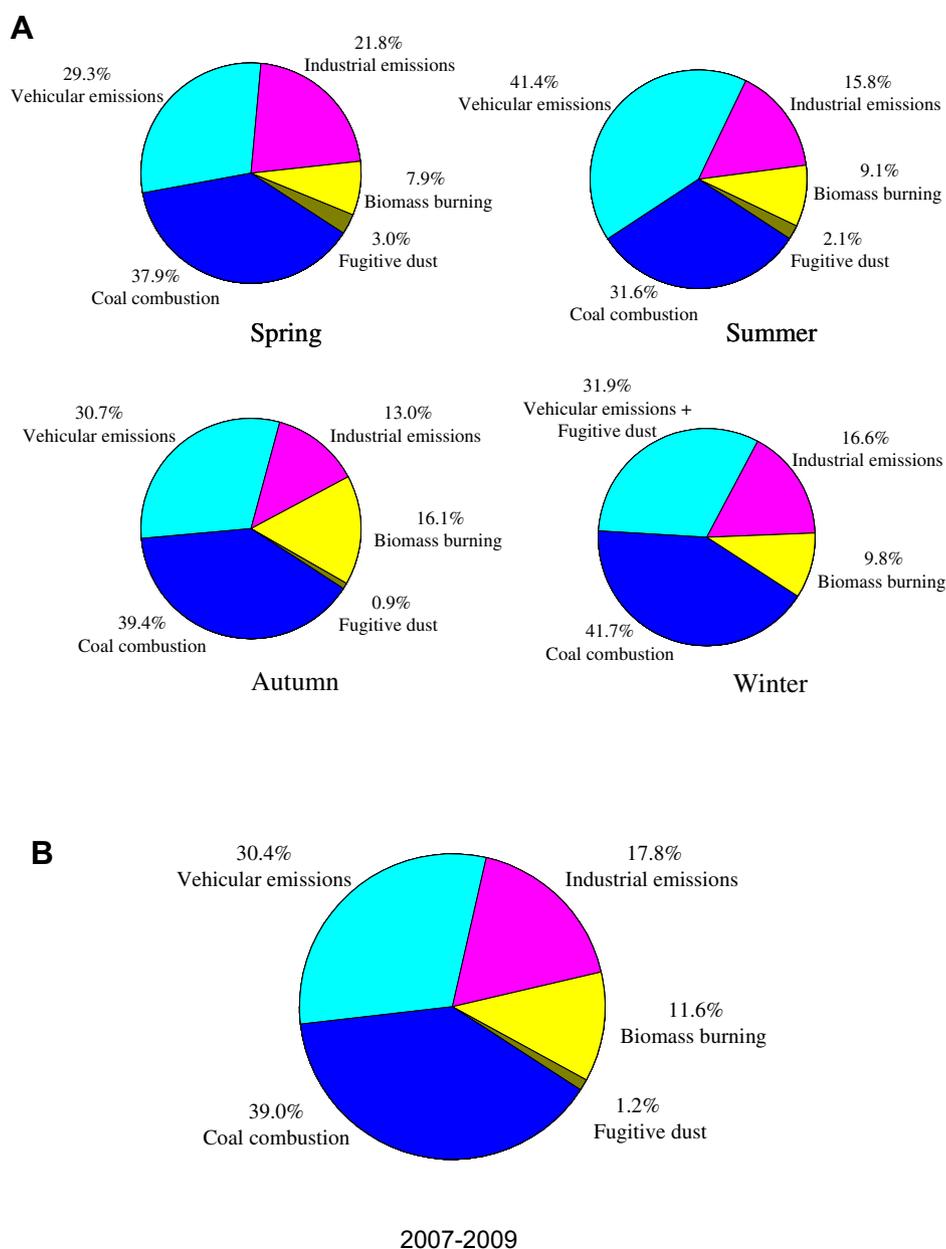


Fig. 3. Source apportionments by Positive Matrix Factorization receptor model for  $PM_{2.5}$  Pb for: (A) each season and (B) average of 2007–2009.

(the average  $^{207}\text{Pb}/^{206}\text{Pb}$  ratio was  $0.843 \pm 0.032$  (conc.  $\pm$  uncertainty);  $^{208}\text{Pb}/^{206}\text{Pb}$  was  $1.908 \pm 0.058$ ) and high in summer ( $^{207}\text{Pb}/^{206}\text{Pb}$  was  $0.860 \pm 0.032$ ;  $^{208}\text{Pb}/^{206}\text{Pb}$  was  $2.039 \pm 0.057$ ). These ratios were consistent with previous studies:  $^{207}\text{Pb}/^{206}\text{Pb}$  ratios were 0.879 in summer of 1987 and 0.866 in winter of 1998 in Beijing (Mukai et al., 1993); Harbin appeared to have the average  $^{207}\text{Pb}/^{206}\text{Pb}$  ratio lower in winter (0.853) than that in summer (0.871) in 1997 (Mukai et al., 2001).

Table 2 showed gasoline vehicle exhaust samples had higher Pb isotope ratios. Zheng et al. (2004) reported  $^{207}\text{Pb}/^{206}\text{Pb}$  ratio of 0.885 and  $^{208}\text{Pb}/^{206}\text{Pb}$  ratio of 2.145 for vehicle exhaust samples in Shanghai. Chinese coal has been reported to have wide variations in Pb isotope ratios (Mukai et al., 1993). However, coal combustion samples showed lower  $^{207}\text{Pb}/^{206}\text{Pb}$  ratios (from 0.828 to 0.877) than those of vehicle exhaust samples (from 0.862 to 0.911). Average  $^{207}\text{Pb}/^{206}\text{Pb}$  ratio for Northern China coal ranged from 0.84 to 0.86, with an average of 0.847 (Mukai et al., 2001).

Average  $^{207}\text{Pb}/^{206}\text{Pb}$  ratio in winter ( $0.843 \pm 0.032$ ) was similar to coal combustion source samples (from 0.847 to 0.860), confirming the impact of the coal combustion on atmospheric  $\text{PM}_{2.5}$  Pb concentrations. The summer ratios ( $0.860 \pm 0.032$  and  $2.039 \pm 0.057$ ) were close to  $^{207}\text{Pb}/^{206}\text{Pb}$  (from 0.862 to 0.901) and  $^{208}\text{Pb}/^{206}\text{Pb}$  (from 2.085 to 2.194) ratios of vehicle exhaust samples, except for the leaded gasoline collected in Shanghai (0.901 for  $^{207}\text{Pb}/^{206}\text{Pb}$  and 2.194 for  $^{208}\text{Pb}/^{206}\text{Pb}$ ). These indicated that vehicular emission was the major Pb source during summer in Xi'an. In Tianjin (Wang et al., 2006), isotope ratios gradually reduced from 0.870 in 1994 to 0.863 in 2001 for  $^{207}\text{Pb}/^{206}\text{Pb}$  and from 2.136 in 1994 to 2.116 in 2001 for  $^{208}\text{Pb}/^{206}\text{Pb}$ . The reductions in ratios correlated well with national statistical data of leaded and unleaded petrol productions (Wang et al., 2006).

### 3.3.4. Source apportionment by positive matrix factorization (PMF) model

The three years  $\text{PM}_{2.5}$  data including 17 chemical species were included in the PMF analyses (i.e., OC, EC, As, Br, Cd, Ca, Cl, Cr, Fe, K, Mn, Mo, Ni, S, Ti, Zn, and Pb). The profiles of each factor and factor loadings were shown in Fig. S5 and Fig. 3. The frequency distribution of scaled residuals was taken into account, most of which were between  $-2$  and  $+2$ , ensuring a good agreement between the PMF model results and the input data.

The PMF analyses indicated that coal combustion was the largest contributor (39.0%) to  $\text{PM}_{2.5}$  mass concentrations during 2007–2009, and this factor was dominated by S, OC, EC, and As. Contributions of coal combustion reached 41.7% in winter, 39.4% in autumn, 37.9% in spring, and 31.6% in summer, consistent with variations in ambient  $\text{PM}_{2.5}$  Pb level.

The second PMF factor had high loadings for OC, EC, Zn, Pb, and Br, which was best explained by emissions from motor vehicles, accounting for 30.4% of annual  $\text{PM}_{2.5}$  mass, and 41.4% during summer. Even though Pb was no longer an additive in gasoline, Pb is still found in the crude oil, with a concentration of the order of  $10^{-15}$  mg  $\text{L}^{-1}$  (Pacyna, 1998). Several studies have shown that vehicular emissions are still an important source of atmospheric Pb and Br in China (Li et al., 2009a, 2009b).

Zn is found in the exhaust from motor vehicles, and it is also found in tyre wear particles, but not at a high level (Wang et al., 2008). Metallurgical processes produce most of Zn (Bennet et al., 2005; Kulshrestha et al., 2009). The Zn concentrations in the profiles of this factor were very high, mostly attributing to industrial emissions. High loadings for Factor 3 were also found for OC, EC, S, and Cl. Industrial emissions accounted for 17.8% of the annual average in  $\text{PM}_{2.5}$  mass with a slight variation among seasons, ranging from 13.0% (for autumn) to 21.8% (for spring).

OC and K are commonly used as markers of biomass burning (Wang et al., 2008; Xie et al., 2008) as shown in Factor 4. Xi'an is surrounded by farmlands and subjected to biomass burning of crop residues, especially in autumn. The contribution accounted for 16.1% of  $\text{PM}_{2.5}$  mass in autumn, which was much higher than that in other seasons (8–10%).

Factor 5 was enriched in crustal elements (e.g. Ca, Fe, Ti, and Mn), representing mineral aerosol and fugitive dust. This source accounted for only 1.2% of  $\text{PM}_{2.5}$  mass. This factor analysis supported the results of the EF calculations, showing that most of atmospheric Pb was from non-crustal sources.

## 4. Conclusions

Daily  $\text{PM}_{2.5}$  samples were collected from 1 January 2007 to 31 December 2009 in Xi'an, China. In addition to  $\text{PM}_{2.5}$  mass, samples were submitted for carbon (OC, EC, and carbon fractions), elements (S, Cl, K, Ca, Ti, Cr, Mn, Fe, Ni, Zn, As, Br, Mo, Cd, and Pb) and Pb isotope ( $^{204}\text{Pb}$ ,  $^{206}\text{Pb}$ ,  $^{207}\text{Pb}$ , and  $^{208}\text{Pb}$ ) analyses. This information was especially important for evaluating the changes in  $\text{PM}_{2.5}$  Pb concentrations that have occurred since the phasing out of leaded gasoline in Xi'an, 2000.

Average  $\text{PM}_{2.5}$  Pb concentration was  $0.306 \mu\text{g m}^{-3}$ ; the highest seasonal Pb concentrations were observed in winter, with the highest daily concentration of  $2.631 \mu\text{g m}^{-3}$  found on 21 January 2007. The  $^{207}\text{Pb}/^{206}\text{Pb}$  ratios (average of  $0.843 \pm 0.032$ ) in winter samples were similar to those found in coal combustion samples (0.847–0.860), indicating that coal combustion was the most important source of Pb in winter. The average  $^{207}\text{Pb}/^{206}\text{Pb}$  and  $^{208}\text{Pb}/^{206}\text{Pb}$  ratios of  $0.860 \pm 0.032$  and  $2.039 \pm 0.057$  in summer samples were all similar to the ratios of vehicle exhaust samples (0.862–0.901 and 2.085–2.194, respectively), suggesting that vehicular emissions contributed the most  $\text{PM}_{2.5}$  Pb in summer in Xi'an.

Sources of  $\text{PM}_{2.5}$  Pb are further investigated through the use of EPA PMF 3.0 model. PMF produced five factors that contributed to  $\text{PM}_{2.5}$  mass: coal combustion, vehicular emissions, industrial emissions, biomass burning, and fugitive dust. Coal combustion was the largest contributor, accounting for 39.0% of  $\text{PM}_{2.5}$  mass, followed by motor vehicle emissions (30.4%). During the cold winter season, ambient  $\text{PM}_{2.5}$  mass concentrations were dominated by coal combustion (41.7%); but during the warm summer season,  $\text{PM}_{2.5}$  mass concentrations were dominated by vehicular emissions (41.4%), consistent with seasonal  $\text{PM}_{2.5}$  Pb variations.

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## Appendix. Supplementary information

Supplementary data related to this article can be found online at doi:10.1016/j.atmosenv.2011.09.078.

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