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Comprehensive Study of Lead Pollution in Shanghai by Multiple Techniques

M. G. Tan,† G. L. Zhang,*,† X. L. Li,† Y. X. Zhang,† W. S. Yue,† J. M. Chen,† Y. S. Wang,† A. G. Li,† Y. Li,† Y. M. Zhang,‡ and Z. C. Shan‡

Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201800, China, and Shanghai Environment Monitoring Center, Shanghai 200030, China

Aerosol samples of PM_{10} particulates were examined with particle-induced X-ray emission (PIXE and micro-PIXE), inductively coupled plasma-mass spectrometry, and X-ray absorption fine structures (XAFS) to investigate atmospheric Pb concentrations and its chemical species and to decide the source assignment. From the elemental analyses, lead concentrations were averaged at 369 and 237 ng·m^{-3} in aerosol samples of PM_{10} collected from 19 monitor sites in Shanghai in the winter of 2002 and 2003, respectively. The XAFS results show that major chemical forms of the lead particulates are probably $PbCl_2$, $PbSO_4$, and PbO. A calculation of isotope ratio and chemical mass balance of the PM_{10} samples revealed that the atmospheric lead particulates in Shanghai in the two periods were mainly from coal combustors, iron and steel plants, and automobile exhausts, with coal combustion dominating the lead pollution after the phasing out of leaded gasoline in 1997 in Shanghai.

Inhaled fine particulates are known to have serious adverse impacts on human health. Smaller size particulate matter, which goes deeper into the lung, is of particular concern. $PM_{2.5}$, particulate matter of less than 2.5 μm in size, can well reach the alveolus and penetrate the bloodstream.[1,2] Especially, the lead contents in $PM_{2.5}$, or PM_{10} sometimes, may affect young children, and even the fetuses, as low doses of lead exposure may cause learning problems and may reduce the intelligence quotient (IQ). It was reported that the IQ fell 4−7 points with an increase of 10 μg/100 mL in lead blood level,[3−5] and anemia and neurological impairments of the children, such as seizures, mental retardation, and behavioral disorders, could be related to excessive exposure to lead.[6,7] According to a report from the Research Center of Aquatic Pathology, University of Maryland, USA, 35% of children in American cities suffered elevated blood lead levels referring to the value of 10 μg/100 mL recommended by the U.S. CDC, though 10 μg/100 mL lead content in the blood is dangerous by criteria nowadays, from which researchers in China were seriously concerned over a survey in the cities of Xi'an, Shenyang, and Beijing that 85% of the children had abnormally high blood lead levels before leaded gasoline was phased out in 1997 in China.[8]

In Shanghai, a city with a population of over 16 million, special concerns are paid over its atmospheric quality, which has been affected in particular by coal combustion and vehicle exhaust emissions. In 2002, 5 years after phasing out leaded gasoline, the average blood lead of children in Shanghai was ~7.6 μg/100 mL, with 24.8% of the children being over 10 μg/100 mL.[9] As is well known, blood lead levels were closely correlated to aerosol lead concentrations,[10−13] so it is important to investigate aerosol lead concentrations (especially in air particulate matter) and their original sources after the phasing out of leaded gasoline, even though it could be a difficult task in terms of influential factors as, for example, the sites, season, temperature, humidity, rainfall, wind direction, and strength of the aerosol sampling.

Based on our micro-particle-induced X-ray emission (PIXE) analysis of aerosol samples in the past a few years for percentage contributions of particle numbers from different emission sources in Shanghai,[14−16] a comprehensive study of lead pollution in Shanghai was carried out with PIXE, micro-PIXE, inductively

* Corresponding author. Telephone: (086)21-59554768. Fax: (086)21-59553021. E-mail: glzhang@sinap.ac.cn.

† Shanghai Institute of Applied Physics.

‡ Shanghai Environment Monitoring Center.

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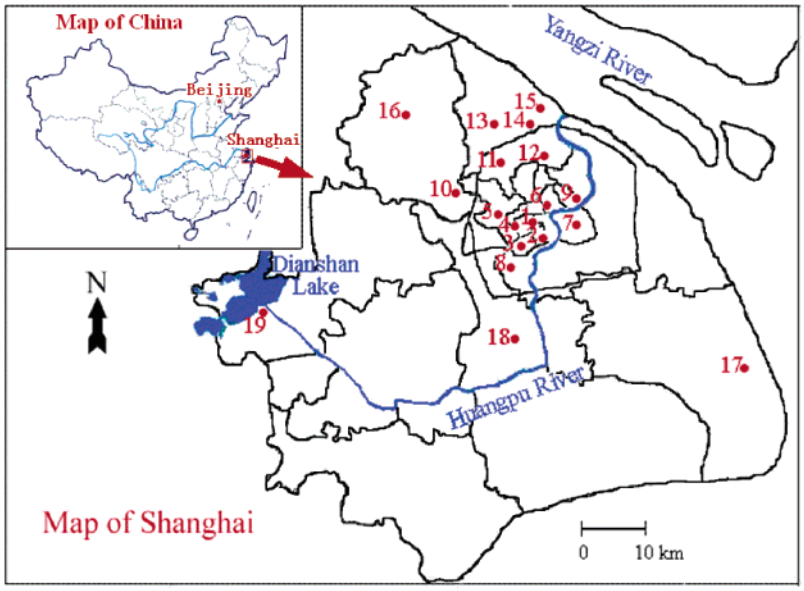

Figure 1. Locations of the sampling sites in Shanghai. (1) Guang Chang (GC); (2) Lu Wan (LW); (3) Kang Pin (KP); (4) Jin An (JA); (5) Pu Tuo (PT); (6) Hong Kou (HK); (7) Pu Dong (PD); (8) Xu Hui (XH); (9) Yang Pu (YP); (10) Dao Pu (DP); (11) Hu Ma (HM); (12) Song Nan (SN); (13) Yang Hang (YH); (14) Gang Yan (GY); (15) Wu Song (WS); (16) Jia Ding (JD); (17) Nan Hui (NH); (18) Ming Hang (MH); (19) Qing Pu (QP).

coupled plasma-mass spectrometry (ICPMS), and X-ray absorption fine structures (XAFS) for the concentrations, chemical species, and source assignment of Pb in the PM_{10} and $PM_{2.5}$ aerosol particles. And a source apportionment could be made by means of individual particle fingerprint, lead isotopic ratio, and chemical mass balance.

EXPERIMENTAL SECTION

Monitoring Sites and Sample Collection. Collaborating with the Environment Monitoring Center of Shanghai, a network of the sampling sites was designed, which is given in Figure 1. The network had 19 sampling sites: Guang Chang (GC), Lu Wan (LW), Kang Pin (KP), Jin An (JA), Pu Tuo (PT), Hong Kou (HK), Pu Dong (PD), Xu Hui (XH), Yang Pu (YP), Dao Pu (DP), Hu Ma (HM), Song Nan (SN), Yang Hang (YH), Gang Yan (GY), Wu Song (WS), Jia Ding (JD), Nan Hui (NH), Ming Hang (MH), and Qing Pu (QP), covering all the urban and suburb areas and including major industrial zones, residential areas, heavy traffic regions, and locations with clean air as well. The aerosol samples were collected in both winter (December 2002 to January 2003, and December 2003 to January 2004) and summer seasons (July to August 2003) in order to investigate seasonal variations of the lead levels. The sampling, lasted for about three weeks, was performed on fine and breezy days with the temperatures being almost the same.

TEOM1400n and TEOM2100 sampling systems, made by Rupprecht & Patashnick Co. Inc., were used to collect PM_{10} and $PM_{2.5}$ particles. Cellulose filters of 47 mm in diameter with 0.45-μm pore size (Millipore Co. Ltd.) were used. PM_{10} particles in seven monitoring sites were collected with TEOM1400n samplers at a flow rate of 15.6 L/min, and PM_{10} particles in the other monitoring sites were collected with the TEOM2100 portable sampler at a flow rate of 5 L/min. $PM_{2.5}$ particles were collected with the TEOM2100 portable samplers deployed at all 19 sites. The samplers were calibrated with each other before and after the sampling. A total of 106 environmental monitor samples were collected, with each of the samples being collected in 24−48 h at 10−15 m above the ground.

Emission Source Samples. PM_{10} and $PM_{2.5}$ were collected at different emission sources. They included 6 soil samples, 14 cement samples, 6 coal combustion samples (3 from power plants and 3 from boilers), 5 vehicle exhausts samples from leaded gasoline and 5 from unleaded gasoline, and 7 dust samples from iron and steel plants. In addition, coal samples were collected from different suppliers in Shanghai. The emission source sampling was in collaboration with the Environment Monitoring Center of Shanghai, which authorized the exhaust stacks or special installations for the sample collections. The soil, cement, and coal samples were ground into powders at Shanghai Institute of Applied Physics (SINAP), Chinese Academy of Sciences. The powder size has no observable effect on Pb concentration, as it distributed homogeneously in the materials.

PIXE and μ-PIXE. Particle-induced X-ray emission is a common nuclear method for trace element analysis.[17] Proton beams of a few million electronvolts (MeV) are often used to produce characteristic X-rays from the atoms in the sample under investigation, to analyze quantitatively the elements by X-ray spectra. A proton beam can be focused down to micrometer sizes to form a proton microprobe, or μ-PIXE.[18] In this work, elemental analysis of single PM_{10} particles was performed at SINAP on the 4UH Pelletron accelerator with its proton microprobe, which comprises a microbeam-forming system and a SUN-S10 computer-based MPSYS data acquisition system. A Si (Li) detector (Ortec) with an energy resolution of 150 eV at 5.9 keV and an active area of 70 mm^2 was applied for detecting the X-rays. Protons of 3 MeV were focused to 2-μm spot size with typically 100−200 pA beam

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current. A 30 nC integrated beam charge was required for measuring a PM_{10} sample, which is characterized by its μ-PIXE spectra, hence its fingerprint. An algorithm of pattern recognition was applied to identify original sources of the PM_{10} particles by measuring a few hundreds of PM_{10} particles from the monitoring sites and emission sources, respectively.[19] According to the pattern recognition algorithm, the μ-PIXE spectra can be treated as an n-component column vector in an n-dimensional Euclidean space. If the Euclidean angle (θ) between two spectrum vectors is small enough, the two μ-PIXE spectra are considered similar. The discriminative function is defined as follows:

$$\cos\theta = \vec{\chi}'\cdot\vec{y}/[(\vec{\chi}'\cdot\vec{\chi})(\vec{y}'\cdot\vec{y})]^{1/2}$$

where $\vec{\chi}'$ and $\vec{y}'$ are transpositions of $\vec{\chi}$ and $\vec{y}$, respectively. The degree of similarity of two μ-PIXE spectra is described by $\cos\theta$, which is close to 1 for two spectra with similar features.

XAFS Spectroscopy. XAFS is a powerful technique to study chemical species.[20] An atom has its X-ray absorption edge, and different chemical species of the element are different with their fine structures at the absorption edge. Therefore, XAFS performed on a synchrotron radiation facility, which provides high-intensity monochromatic X-rays, can be completed conveniently with results of high precision. The XAFS study was conducted on Beijing Synchrotron Radiation Facility (BSRF), which runs pulsed electron beams of 2.2 GeV in energy in the storage ring with an average beam current of ~100 mA. The lead absorption was measured on the XAFS station with a double crystal monochromator of Si-(111), by which monochromatic X-rays of 12 914−13 350 eV could be selected for Pb L-edge absorption measurements. About 200 measurements were done in the energy range, and each measurement took 3−4 s.

ICPMS. The technique of lead isotope ratios is a reliable method for studying lead origin in the atmosphere.[21] The lead concentrations and isotope ratios were analyzed by an inductively coupled plasma mass spectrometer (X-7; Thermo-Elemental Inc.). Indium was added to digests of the particle samples as an internal standard, and multielemental standard solutions (SPEX Certiprep Inc.) were used to prepare calibration solutions. National Institute of Standards and Technology (NIST, Gaithersburg, MD) NIST 981 reference material was used to determine mass bias correction factors of isotope ratios. The experimental details on the measurement were given in our previous work.[22] Briefly, the digested samples were measured for elemental concentrations, and then the lead content in solution was adjusted in the range of 5−25 ng mL^{-1} by appropriate dilution using 1% HNO_3 prior to the measurement of lead isotope ratios. Analytical blank was also handled in the same way, and it was usually negligible (<0.01 ng mL^{-1}) compared with the lead levels in samples.

The emission source samples of cements, coal ashes, metallurgic dusts, gasoline, and soils were prepared in accordance with ref 16. A high-pressure microwave digestion system (Ethos 320; Milestone, Italy) was employed with a modified Milestone digestion program to treat the samples. The nitric acid, hydrogen peroxide, and hydrofluoric acid used in the sample preparation were of ultrapure grade. And the HNO_3 was further purified by using a sub-boiling assembly made of perfluoroalkoxy copolymer. A digested solution was evaporated by the HF digestion procedure in a Teflon beaker at 150 °C and reduced to a small drop of liquid residue, which was dissolved with 2% HNO_3 for ICPMS analysis. Ultrapure water (>18.2 MΩ/cm) from a Milli Q system (A10, Millipore) was used for preparing the solutions and rinsing the vessels.

RESULTS AND DISCUSSION

Variation of Pb Concentration in Particulate Matter. Averaged Pb concentrations measured by PIXE in the PM_{10} and $PM_{2.5}$ samples collected in winter of 2002 are 369 ± 74 and 196 ± 40 ng·m^{-3}, respectively (Table 1). The Pb concentrations at the industrial areas, e.g., 1605 and 715 ng·m^{-3} in PM_{10}, and 650 and 510 ng·m^{-3} in $PM_{2.5}$, respectively at the GY and YP sites, were much higher than the suburban areas, e.g., 135 and 175 ng·m^{-3} in PM_{10} and 46 and 85 ng·m^{-3} in $PM_{2.5}$, respectively, at the QP and JD sites. From the average mass concentrations and lead concentrations of $PM_{2.5}$ and PM_{10} collected at all the monitoring sites, the mass concentration ratio of $PM_{2.5}$ to PM_{10} and lead concentration ratio of $PM_{2.5}$ to PM_{10} could be calculated. Within the measurement error, no significant difference was observed between the two ratios in the winter of 2002. However, analysis of the PM samples collected in the winter of 2003 showed that averaged mass concentrations of the PM_{10} and $PM_{2.5}$ samples were 140 ± 13 and 82 ± 8 μg·m^{-3}, respectively, and averaged Pb concentrations were 224 ± 45 and 185 ± 37 ng·m^{-3}, respectively (Table 2). Therefore, the mass concentration ratio was 0.59 and the lead concentration ratio of $PM_{2.5}$ to PM_{10} was 0.83. And this indicates that the ambient lead was concentrated in the fine fraction and could be linked to the variations in atmospheric emission inventories.

According to ref 16, the average lead concentrations of PM_{10} in winter of 1997 and 2001 were respectively 466 ± 250 and 515 ng·m^{-3}, which are higher than winter of 2002, and much higher than winter of 2003, indicating a decreasing atmospheric lead concentration (Figure 2) after phasing out of leaded gasoline in Shanghai in 1997. On the other hand, as shown in Table 2, the lead concentration in winter 2003 was higher than in 2003. This would be obvious, as coal consumption is higher in winter. It should be noted that the lead concentration of PM_{10} in Shanghai is much higher than Hong Kong and Tokyo, where the lead concentration of PM_{10} is just 14−190 and 64.4 ng·m^{-3} respectively.[23−24]

Chemical Species of Pb. Atmospheric particulate matter is a complex mixture, in which an element can be in the presence of different chemical compounds. With the XAFS technique, we were able to determine chemical species of the lead. Based on knowledge of possible Pb species in the atmosphere, we chose $PbSO_4$, PbO, PbO_2, $PbCO_3$, $Pb_3(PO_4)_2$, and $PbCl_2$ as reference materials. As the Pb concentrations in $PM_{2.5}$ and PM_{10} samples

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Table 1. Mass Concentrations (MC) and Pb Concentrations (PC) of $PM_{2.5}$ and PM_{10} in Winter of 2002

sampling sites	MC of PM_{10} ($mg \cdot m^{-3}$)	PC of PM_{10} ($mg \cdot m^{-3}$)	MC of $PM_{2.5}$ ($mg \cdot m^{-3}$)	PC of $PM_{2.5}$ ($mg \cdot m^{-3}$)	$C_M(PM_{2.5})/C_M(PM_{10})$	$C_{Pb}(PM_{2.5})/C_{Pb}(PM_{10})$
GC	0.347	476 ± 19	0.179	408 ± 14	0.52	0.86
LW	0.151	468 ± 25	0.128	327 ± 11	0.85	0.70
KP	0.111	127 ± 10	0.089	57 ± 3	0.80	0.45
JA	0.103	132 ± 9	0.060	56 ± 3	0.58	0.42
PT	0.074	88 ± 4	0.063	52 ± 2	0.85	0.59
HK	0.085	137 ± 12	0.059	116 ± 10	0.69	0.85
PD	0.119	210 ± 12	0.089	169 ± 11	0.75	0.81
XH	0.294	520 ± 28	0.226	156 ± 7	0.77	0.30
YP	0.130	715 ± 45	0.049	510 ± 24	0.38	0.71
DP	0.233	190 ± 11	0.101	55 ± 4	0.43	0.29
HM	0.389	540 ± 14	0.186	295 ± 8	0.48	0.55
SN	0.327	430 ± 15	0.125	285 ± 6	0.38	0.66
YH	0.152	530 ± 23	0.076	280 ± 15	0.50	0.53
GY	0.235	1605 ± 85	0.144	650 ± 41	0.61	0.41
WS	0.104	390 ± 18	0.033	255 ± 13	0.32	0.58
JD	0.092	175 ± 7	0.067	85 ± 3	0.73	0.49
NH	0.205	245 ± 10	0.088	175 ± 7	0.43	0.71
MH	0.288	305 ± 19	0.227	75 ± 5	0.79	0.25
QP	0.148	135 ± 7	0.089	46 ± 3	0.60	0.34

Table 2. Lead Concentrations of PM_{10} in Summer and Mass and Lead Concentrations of PM_{10} and $PM_{2.5}$ in Winter of 2003

	summer	winter					
sampling sites	PC of PM_{10} ($ng \cdot m^{-3}$)	MC of PM_{10} ($ng \cdot m^{-3}$)	PC of PM_{10} ($ng \cdot m^{-3}$)	MC of $PM_{2.5}$ ($ng \cdot m^{-3}$)	PC of $PM_{2.5}$ ($ng \cdot m^{-3}$)	$C_M(PM_{2.5})/C_M(PM_{10})$	$C_{Pb}(PM_{2.5})/C_{Pb}(PM_{10})$
PT	67 ± 20	0.148	104 ± 13	0.083	90 ± 12	0.56	0.87
JA	176 ± 19	0.131	108 ± 16	0.090	114 ± 16	0.69	1.05
HK	111 ± 13	0.124	118 ± 15	0.063	63 ± 10	0.51	0.53
YP	127 ± 18	0.115	225 ± 29	0.079	233 ± 25	0.68	1.03
LW	81 ± 12	0.117	260 ± 27	0.071	453 ± 68	0.61	1.74
KP	25 ± 4	0.239	389 ± 54	0.149	302 ± 48	0.62	0.78
XH	144 ±19	0.149	165 ± 25	0.131	354 ± 46	0.88	2.15
WS	97 ± 14	0.052	328 ± 49	0.031	143 ± 26	0.59	0.43
GY	129 ± 17	0.139	315 ± 35	0.070	266 ± 29	0.50	0.84
SN	145 ± 23	0.133	272 ± 28	0.071	201 ± 23	0.54	0.74
HM	149 ± 17	0.140	236 ± 34	0.060	373 ± 56	0.43	1.58
YH	81 ± 12	0.117	308 ± 40	0.073	199 ± 21	0.62	0.64
NH	76 ± 11	0.042	243 ± 23	0.025	112 ± 17	0.59	0.46
MH	231 ± 30	0.162	283 ± 45	0.093	241 ± 32	0.58	0.85
QP	64 ± 9	0.121	201 ± 26	0.069	113 ± 18	0.57	0.56
DP	220 ± 35	0.156	95 ± 11	0.076	141 ± 27	0.49	1.49
JD		0.065	104 ± 12	0.029	97 ± 13	0.44	0.93
GC		0.240	368 ± 51	0.126	97 ± 15	0.53	0.26
PD		0.153	382 ± 42	0.078	90 ± 11	0.51	0.24

were low with respect to sensitivity of the XAFS measurement (in spite of a few thousand ppm Pb in some of the samples), the fluorescence yield mode was used for the XAFS measurements, whereas the conventional transmission mode was used for the reference samples, in which the Pb concentrations were high.

Pb L_{III}-edge XAFS spectra of the PM_{10} and $PM_{2.5}$ samples collected at GC, NH, and GY (Figure 3) are quite similar to one another, indicating that Pb contents in the samples of different particle sizes and from different sites were of similar chemical components. However, all the XAFS spectra of the PM samples are different from any spectra of the reference samples (Figure 4), suggesting that several Pb compounds may coexist in the PM samples. From the fact that the XAFS spectra of PbO_2 differed from the PM spectra the most, one could know that PbO_2 (Pb^{4+}) did not exist in the particulate matter.

Assuming that there are k lead components in a sample, the absorption coefficient of Pb in the sample shall be a sum of the absorption coefficient of each component. Therefore, at i experimental point of the XAFS, the Pb absorption coefficient A_i can be expressed as,

$$A_i = C_1 a_{i1} + C_2 a_{i2} + \cdots + C_k a_{ik} \quad (1)$$

where a_{i1}, a_{i2} ... a_{ik} stand for absorption coefficient of each component, C_1, C_2 ... C_k are their relative concentration (atom percent).

This system's regression analysis, which is based on least-squares fitting, can be used to calculate relative concentrations for each component. In this work, the independent variable of the regression equation is the absorption coefficient of a reference

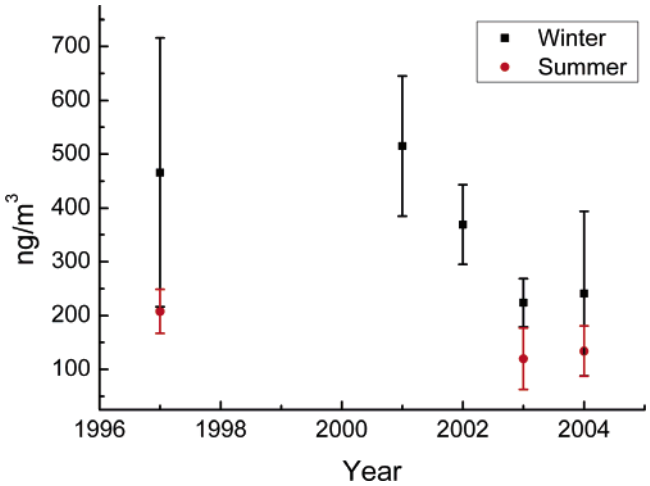

Figure 2. Seasonal averaged Pb concentrations in PM10 of Shanghai.

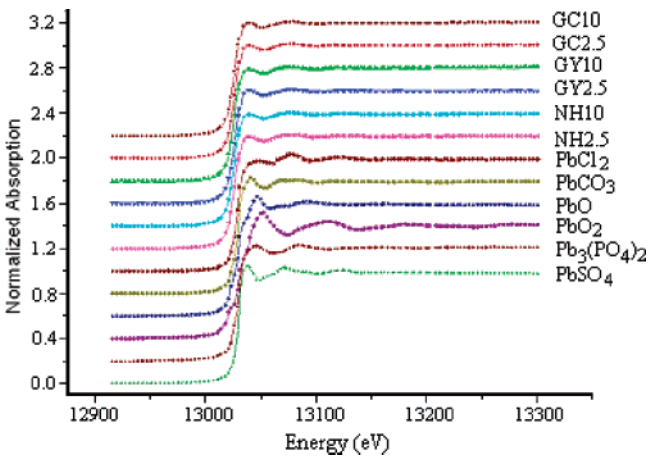

Figure 3. Pb L_L-edge XAFS spectra of the $PM_{2.5}$ and PM_{10} samples collected from GC, GY, and NH and reference samples of $PbCl_2$, $PbCo_3$, PbO, PbO_2, $Pb_3(PbO4)_2$, and $PbSO_4$.

sample, the dependent variable is absorption coefficient of a PM sample, and the coefficient of the regression equation is the relative concentration of each component.

The experimental data were treated by NSRLXAFS, the software for background reduction and data normalization developed by the National Synchrotron Radiation Laboratory, University of Science and Technology of China, before the relative concentrations of each component were calculated using regression analysis in EXCEL.

Typical results of the regression from Pb L_{III}-edge XAFS data of the PM_{10} sample collected at GC are given in Figure 4. The regression was done with linear combinations of the spectra of $PbCl_2$, $PbSO_4$, and PbO reference compounds, as the best fit was obtained between the PM_{10} spectra and regression spectra by assuming that Pb species in the PM were $PbCl_2$, $PbSO_4$, and PbO (Figure 4). The results of regression analysis indicated that relative concentrations of $PbCl_2$, $PbSO_4$, and PbO in the sample were 41 $\pm$ 4, 37 $\pm$ 2, and 22 $\pm$ 3%, respectively. The larger $PbCl_2$ and $PbSO_4$ percentage concentrations in the PM particles in Shanghai are understandable. It is well known that lead in soil and minerals exists generally in a bivalence state in inorganic compounds of anglesite [$PbSO_4$], cerrusite [$PbCO_3$], and PbS, rather than elemental lead.[25] Concentrations of the lead species in aerosol

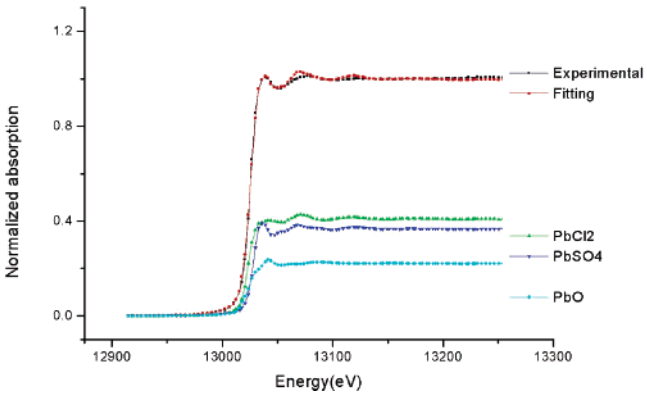

Figure 4. Pb L_L-edge XAFS spectra of PM_{10} collected at GC, and the data fitting with a combination of reference spectra of $PbCl_2$, $PbSO_4$, and PbO.

particles, however, may differ from their concentrations in soil and minerals, because aerosol particles in cities are mainly contributed by anthropogenic activities, and just a minor part of the aerosol particles stems from natural soil and minerals. In Shanghai, it is estimated that over 500 thousand tons of sulfur dioxide are exhausted into air annually; hence, a high atmospheric SO_2 concentration of ~0.068 mg/m^3 and an annual average pH value of 5.7 in the air,[26] which may well provide conditions to convert lead oxides into lead sulfate. In addition, Shanghai is a coastal city, where it is easy to form chloride aerosols.

Source Apportionment of Lead Pollution in Atmospheric Aerosol Particles. In 1999, two years after phasing out of leaded gasoline in Shanghai, an identification of lead pollution sources was carried out by single aerosol fingerprints via a pattern recognition algorithm.[15] It found that major origins of the lead in PM_{10} of Shanghai were cement, automobile exhaust, coal combustion, and metallurgic dusts. However, the study provided just percentages of the lead-contaminated particles, rather than concentrations contributed by different sources. With our results of PM particle analyses and the technique of lead isotope ratio determination, we were able to find that vehicle exhaust particles contributed ~20% of the atmospheric lead in mass concentration in Shanghai in 2001.[16]

In 2002, based on single aerosol particle studies with the μ-PIXE and pattern recognition technique, we found that just 3% of lead-contaminated particles in the atmosphere of GC in Shanghai was of cement origin, instead of 40% in 1999.[15] This could be attributed to technological improvements in Shanghai, where mixed concrete is now sent to construction sites by special suppliers, instead of on-site concrete mixing in the past decades, hence a much reduced cement pollution. The study also showed that the contribution from leaded gasoline decreased markedly in both the downtown and industrial areas; e.g., it dropped from 18 to 0% in GC and to 1% in WS industrial area. This indicates that environmental impact from leaded gasoline was efficiently removed after phasing out of leaded gasoline in Shanghai.

The average lead concentrations of PM_{10} from 19 monitoring sites and the average contribution of each emission source in particle percentage (particle number of an emission source divided

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(26) Yang, X.; Gao, Y. *Shanghai Environ. Sci.* **1999**, *293*.

Table 3. Concentrations (in $\mu g \cdot g^{-1}$) and Isotopic Ratios of Pb in PM_{10} and Emission Source Samples

descriptions	Pb concns	$^{207}Pb/^{206}Pb$	$^{208}Pb/^{206}Pb$	PR[a]
PM_{10}	3077 ± 60	0.8590 ± 0.0010	2.1060 ± 0.0032	
vehicle exhaust (leaded)	7804 ± 160	0.9009 ± 0.0051	2.1938 ± 0.0073	<1
vehicle exhaust (lead free)	238 ± 5	0.8715 ± 0.0042	2.1240 ± 0.0061	30
coal combustion	1788 ± 37	0.8596 ± 0.0023	2.1111 ± 0.0008	16
metallurgic dust	6140 ± 130	0.8529 ± 0.0029	2.0768 ± 0.0076	27
soil	11.7 ± 0.3	0.8410 ± 0.0020	2.0860 ± 0.0020	15
cement	103 ± 2	0.8598 ± 0.0009	2.1036 ± 0.0018	2
unidentified				9

[a] Percentage ratios of the particles of different origins.

by the number of all emission particles) from GC and WS were listed in Table 3. The contributions from cement and soil were 2 and 15%, respectively. According to ICPMS analysis, lead concentrations in samples of 14 cement products available in Shanghai averaged 103 $\mu g \cdot g^{-1}$, while the lead concentrations in soil samples taken from six typical places in urban and suburb areas of Shanghai in 2004 averaged 11.7 $\mu g \cdot g^{-1}$. Containing rather low lead contents, the cement and soil contributed far less to the air lead particle burden than the coal combustion, metallurgic dust, and vehicle exhaust, which should be concluded as major contributors to the atmospheric lead pollution in Shanghai. Based on the lead concentrations and lead isotopic ratios of $^{207}Pb/^{206}Pb$ and $^{208}Pb^{206}Pb$ in the PM_{10} and the emission source (Table 3), individual contribution of the three pollution sources could be calculated with ternary mixing equations.

Setting K_1, K_2 and $1 - (K_1 + K_2)$ as lead contributions to the atmospheric particulate matter, respectively, of coal combustion, metallurgic dust and vehicle exhaust, R_1, R_2, and R_3 as $^{207}Pb/^{206}Pb$ ratios of the three sources, and C_1, C_2, and C_3 as lead concentrations of the three sources, the equation for the lead isotopic ratios and aerosol mass concentrations can be written as follows.

$$K_1R_1 + K_2R_2 + [1 - (K_1 + K_2)]R_3 = R_{PM10} \quad (2)$$

$$K_1C_1 + K_2C_2 + [1 - (K_1 + K_2)]C_3 = C_{PM10} \quad (3)$$

Referring to Table 3, R_1, R_2, and R_3 are 0.8596 ± 0.0023, 0.8529 ± 0.0029, and 0.8715 ± 0.0042, and C_1, C_2, and $C3$ are 1788 ± 37, 6,140 ± 130, and 238 ± 5 $\mu g \cdot g^{-1}$, respectively. R_{PM10} is 0.8590 ± 0.0010; C_{PM10} is 3077 ± 60 $\mu g \cdot g^{-1}$.

Applying eqs 2 and 3, the percentage contribution to atmospheric lead was around 50, 35, and 15% from coal combustion, metallurgic dust, and vehicle exhaust, respectively. Considering standard deviations of the Pb concentration and Pb isotopic ratios, and their relative deviations for the concentration (~±2%) and isotopic ratios (±0.1−±0.3%), the percentage contribution of coal combustion and metallurgic dust may range from 32 to 69% and from 29 to 41%, respectively, and from 3 to 27% for vehicle exhaust. Comparing the $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ ratios in Table 3, one finds that the ratio of coal combustion is the closest to that of PM_{10}, and the metallurgic dust is the second closest. On the other hand, their lead concentrations are higher than the vehicle exhaust. These mean a sequence of the lead contribution fractions, i.e., $f_{coal} > f_{met} > f_{veh}$. In this calculation, we neglected minor contributions from other pollution sources. The cement, having about the same ratio of $^{207}Pb/^{206}Pb$ as coal combustion though, has very low Pb concentration and particle contribution percentage (Table 3), with which we could estimate that the cement contribution might be less than 1% of coal contribution. And soil should contribute even less, because its $^{207}Pb/^{206}Pb$ ratio is far away from that of PM_{10} and there is even less Pb in it. However, it was difficult to have an accurate estimation of contribution factors from all the emission sources; the calculated contributions for three major emission sources should be regarded as an approximation.

Applying eq 2 to the $^{208}Pb/^{206}Pb$ ratios (Table 3) of coal combustion, metallurgic dust, and vehicle exhaust, together with their contribution percentages gotten from the above calculation, the $^{208}Pb/^{206}Pb$ ratio of PM_{10} was 2.101, agreeing very well with the measurement, by which the $^{208}Pb/^{206}Pb$ ratios of PM_{10} in Shanghai were averaged at 2.106.

From the above results, we can conclude that the biggest lead contributor to the air pollution in Shanghai is coal combustion after phasing out of leaded gasoline in 1997. The city consumes annually ~44 million tons of coal, which has an average lead concentration of 13.6 ± 6.6 $\mu g \cdot g^{-1}$ as we determined from 23 coal samples provided by major suppliers in Shanghai. It was reported that 50% of the lead in a burning coal could accumulate on fine particles flying into the air.[12] This means ~300 tons of annual anthropogenic lead release into the air in Shanghai due to coal combustion. PM_{10} collected at coal combustor sites contained ~1788 $\mu g \cdot g^{-1}$ lead, which is much higher than the coals. This suggests that a lead enrichment process may take place during the combustion.

Lead concentrations of metallurgic dusts emitted from sinters, furnaces, and converters were measured, too, and were averaged at 6104 $\mu g \cdot g^{-1}$. Particle percentage of the metallurgic dusts was 27%, as measured by our single aerosol technique. And metallurgic dust is indeed one of major contributors to the atmospheric lead pollution.

Vehicle exhaust had been a bigger contributor of airborne lead burden when gasoline had added tetraethyllead as an antiknock agent, and a high concentration of 7804 $\mu g \cdot g^{-1}$ was found at that time in vehicle exhaust particle samples. Five years after phasing out of leaded gasoline, lead concentration in vehicle exhaust particle samples was merely 238 $\mu g \cdot g^{-1}$. Although vehicle exhaust particles are still among the major contributors of lead pollution, they contributed far less than the other two sources. Referring to the aerosol $^{207}Pb/^{206}Pb$ ratio of 0.864 for the air-borne particle

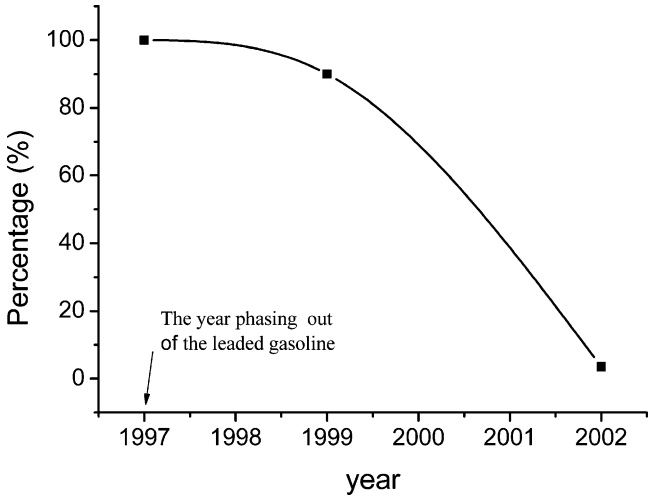

Figure 5. Percentage of leaded gasoline particles in the automobile exhaust articles as a function of years.

sample collected in 1996−1997 in Shanghai by Mukai et al.,[27] and by using the binary mixing equation from Zheng et al.,[16] we could estimate that automobile lead contribution in 1996−1997 was ~30%, which dropped to 20% in 2001−2002,[16] and further dropped in 2002−2003 to 15%, as we found in this study.

According to our measurements of the $^{207}Pb/^{206}Pb$ ratio of atmospheric particulate matter in Shanghai, it dropped from 0.8608 in 1999 to 0.8590 in 2002−2003. However, it was found that the lead concentration (Figure 2) in air and the percentage of lead contribution from the automobile exhaust did not drop immediately after the phasing out of leaded gasoline (Figure 5). Percentage of leaded gasoline particles in total automobile exhaust particle decreased gradually from 1997 to 2002. This may indicate a process of particle cycling takes place between the air and ground.

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CONCLUSIONS

Atmospheric lead contamination, lead species, and source assignment in Shanghai were studied by PIXE, μ-PIXE, ICPMS, XAFS, and other analytical techniques. The results indicate that the lead concentration decreased gradually over the years after phasing out of leaded gasoline in 1997. The atmospheric lead concentration of PM_{10} in the winters of 2002 and 2003 was respectively 369 and 238 ng·m^{-3}, a reduction of 28 and 53% in comparison to 2001. Major species of the lead in the samples collected in winter 2003 were $PbCl_2$, $PbSO_4$, and PbO. Source apportionment of the atmospheric lead was calculated with a combined method of lead isotope ratios and lead mass balance, along with μ-PIXE analysis of single particles and pattern recognition of the spectra. The results suggested that major contributors of atmospheric lead pollution in Shanghai were sequentially coal combustion dust, metallurgic dust, and vehicle exhaust particles. Relative contributions of the air pollution sources were estimated, and for the first time, probably, a metropolitan area is given with a semiquantitative estimation of atmospheric lead contribution from emission sources. To further reduce the lead pollution in Shanghai, it is of the first priority to take measures for controlling emission from coal combustion, now that the contribution from vehicle exhaust particles has decreased rapidly since phasing out of leaded gasoline in 1997, even though particles from the leaded gasoline did not disappear completely in the atmosphere in the following 5 years. Finally, we have demonstrated the power of using the combined analytical techniques of micro-PIXE, ICPMS, and XAFS in studying lead pollution in the atmosphere.

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