

Lead Isotopic Compositions of Selected Coals, Pb/Zn Ores and Fuels in China and the Application for Source Tracing

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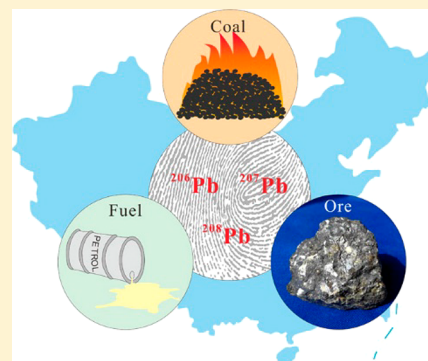
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Supporting Information

ABSTRACT: Lead (Pb) pollution emission from China is becoming a potential worldwide threat. Pb isotopic composition analysis is a useful tool to accurately trace the Pb sources of aerosols in atmosphere. In this study, a comprehensive data set of Pb isotopes for coals, Pb/Zn ores, and fuels from China was presented. The ratios of $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ in the coals were in the range of 1.114–1.383 and 1.791–2.317, similar to those from Europe, Oceania, and South Asia, but different from those from America ($p < 0.01$). The Pb/Zn ores had $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ in 1.020–1.183 and 2.088–2.309, less radiogenic than the coals. Leaded gasolines showed similar Pb isotopic compositions to Pb/Zn ores, with unleaded gasolines and diesels being mixed sources. The average Pb isotopic ratios of gasolines and diesels were significantly different ($p < 0.01$) from those of coals in China, leading to the possibility to discriminate Pb in fuels from in coals. Urban aerosols demonstrated similar Pb isotopic compositions to coals, Pb/Zn ores, and fuels in China. After removing the leaded gasoline, the Pb in aerosols is more radiogenic, supporting the heavy contribution of coal combustion to the atmospheric Pb pollution.



1. INTRODUCTION

Lead (Pb) has been regarded as one of the most toxic metals due to its acutely and chronically adverse effects on humans, especially on children.¹ It can impair the nervous system and ultimately lead to reduced IQ levels.¹ Pb contamination is primarily generated by vehicles, combustion of coals, and smelting of nonferrous metals.^{2–4} After removing the leaded gasoline since 1998, the relative contribution of coals to atmospheric Pb pollution becomes more pronounced in China.^{2,5} As the world's largest producer and consumer of coals,⁶ China is impacted by the increasingly severe Pb pollution due to the large emission of Pb (~46 000 tons during the period of 1990–2009) from coal combustion.² Apart from its detrimental effects upon the domestic ecosystems,^{7–10} Pb pollution from China has been reported as a contributor for the global problems.^{5,11–17}

Due to the stability during physical and chemical processes, Pb isotopes are frequently used as an ideal tool for

characterizing and identifying the sources and pathways of atmospheric Pb pollution.¹¹ Provided the sufficient characteristics of isotopic compositions in a pollutant, anthropogenic sources of Pb could be characterized and identified.^{5,7,10–13,16–18} Unfortunately, limited data for Pb isotopes, especially for coals in China, are available.¹⁸ In the study of Diaz-Somoano et al. (2009),⁵ who investigated the isotopic compositions of Pb in coals from major worldwide coalfields, only one sample was from China. Also, Mukai et al. (1993)¹⁹ reported a few coal samples from Northern China, with Pb isotopic compositions of $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ in 1.114–1.120 and 2.025–2.154. In addition, it was reported that the isotopic compositions of Pb from the coals in China

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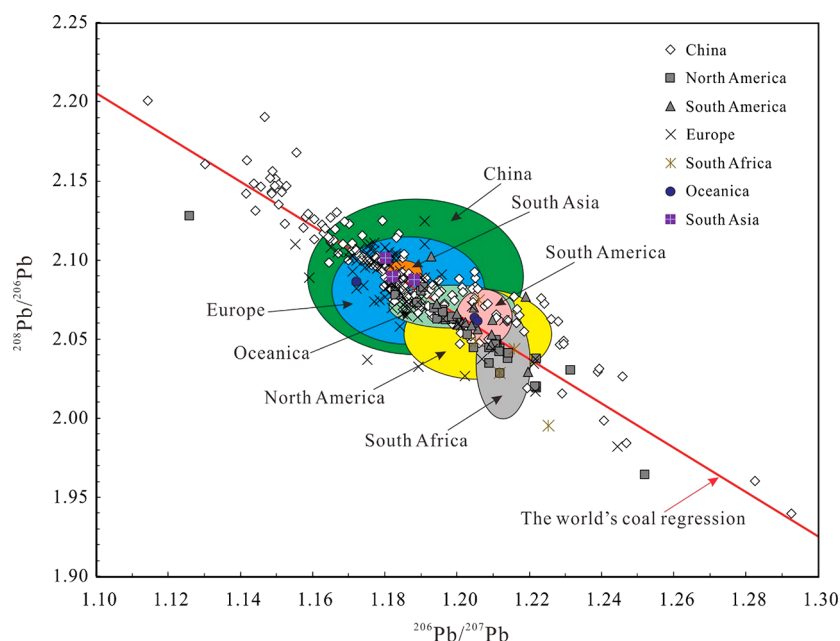


Figure 1. Diagram of $^{206}\text{Pb}/^{207}\text{Pb}$ vs $^{208}\text{Pb}/^{206}\text{Pb}$ in coals from China (data from SI Table S1) and other regions of the world.^{5,21,22} The center, horizontal and vertical axis of ellipses represent the means $\pm 1\text{SD}$ of the $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios.

were similar to those of Pb/Zn ores and automobile emissions.^{11,18} Therefore, it is difficult to discriminate the contribution of coals to the atmospheric Pb pollution in China from other sources without a comprehensive profile of isotopic characteristics of Pb.

In this study, we presented a data set of Pb isotopic compositions for 173 coal samples from major coal mines in China, in comparison with those from fuels and Pb/Zn ores, to create a profile of Pb isotopic compositions for these end members. Based on this information, we conducted a source tracing for Pb in aerosols to screen the temporal and spatial variations of contributors to atmospheric Pb in China in the past two decades. This study would serve as information for tracing atmospheric Pb on a global scale.

2. EXPERIMENTAL SECTION

In this study, 173 coal samples were collected from major coal mines in 18 provinces of China (Supporting Information (SI) Table S1 and Figure S1). The coal mines were selected by their top coal productions in the provinces and covered almost all the large coal basins in China. Coal sample collection is detailed in Zhang et al. (2012).²⁰ In addition, automobile exhaust soot samples were also collected from Hubei and Hainan provinces, China (SI Table S3). After collection, samples were air-dried to a constant weight and pulverized in to 160 meshes ($\sim 100\ \mu\text{m}$ in diameter). Coal samples were further ashed at $400\ ^\circ\text{C}$ in a muffle furnace to a constant weight. Subsamples (50 mg) of coal and exhaust soot were then digested with 2 mL of HNO_3 (65%, v/v) and 1 mL of HF (40%, v/v) in a sealed Teflon beaker at $190\ ^\circ\text{C}$ for 48 h. Upon evaporation to near dried on a hot panel, the samples were then further digested with 1 mL of HNO_3 (65%, v/v) and 0.5 mL of HClO_4 (70%, v/v). After cooling down and diluting to 25 mL with Milli-Q water, the digester was measured for Pb concentration. Reagent blanks, replicates and standard reference materials NIST 1632d (coal) and NIST 1633b (fly ash) were used for quality control; the recoveries of Pb were in 84.2–87.8% for NIST 1632d and in 89.4–93.8% for NIST 1633b, respectively. Prior to quantitation

of Pb isotopes, the digester was diluted to around $30\ \mu\text{g}/\text{g}$ Pb with 2% (v/v) high-purity HNO_3 . A standard reference material NIST SRM981 was used for quality control. The measured ratios of $^{204}\text{Pb}/^{206}\text{Pb}$, $^{206}\text{Pb}/^{207}\text{Pb}$, and $^{208}\text{Pb}/^{206}\text{Pb}$ (0.0591 ± 0.0001 , 1.0931 ± 0.0025 , and 2.1683 ± 0.0045) had good agreement with their respective certifications (0.059042 , 1.0933 , and 2.1681). All the instrumental quantification was performed with a quadrupole plasma-mass spectrometer (Q-ICP-MS) (Agilent 7900, USA).

3. RESULTS AND DISCUSSION

3.1. Isotopic Composition of Pb in Coals. Concentrations of Pb in coals varied from 0.41 to 60.7 mg/kg with an average of 13.7 mg/kg (SI Table S1), comparable to the results of 329 coals from China (range: 0.67–49.3 mg/kg, average: 13.6) reported by the United States Geological Survey (2004).²³ A significantly positive correlation ($p < 0.01$) between Pb concentrations and ash contents in the coals was observed (SI Figure S2), suggesting that the presence of Pb might be influenced by the inorganic minerals (probably clay minerals and pyrite) in the coals.²⁴

The ratios of $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ were in the ranges of 1.114–1.383 and 1.791–2.317 with their respective means and medians at 1.188 and 2.089, and 1.187 and 2.083 (SI Table S1 and Figure 1), reflecting heterogeneous environments of the coalfields in China. However, an obvious geographic distribution pattern of Pb isotopes can be identified (SI Table S1): Coals from Southwestern China (Sichuan, Chongqing, Guizhou, and Yunnan provinces) had the most radiogenic Pb with $^{206}\text{Pb}/^{207}\text{Pb} > 1.20$, followed by Northwestern China (Xinjiang, Gansu, and Shaanxi provinces) and Northeastern China (Heilongjiang province and eastern Inner Mongolia) ($^{206}\text{Pb}/^{207}\text{Pb}$ in 1.19–1.20), whereas, the least radiogenic Pb ($^{206}\text{Pb}/^{207}\text{Pb} < 1.17$) were from North China (Beijing, Hebei, Henan, Shanxi, Shandong and Liaoning provinces, and central Inner Mongolia). The central and Eastern China (Jiangsu, Anhui, and Hunan provinces) had intermediate $^{206}\text{Pb}/^{207}\text{Pb}$ ratios between 1.17 and 1.18. Spatially, the Pb in coals would

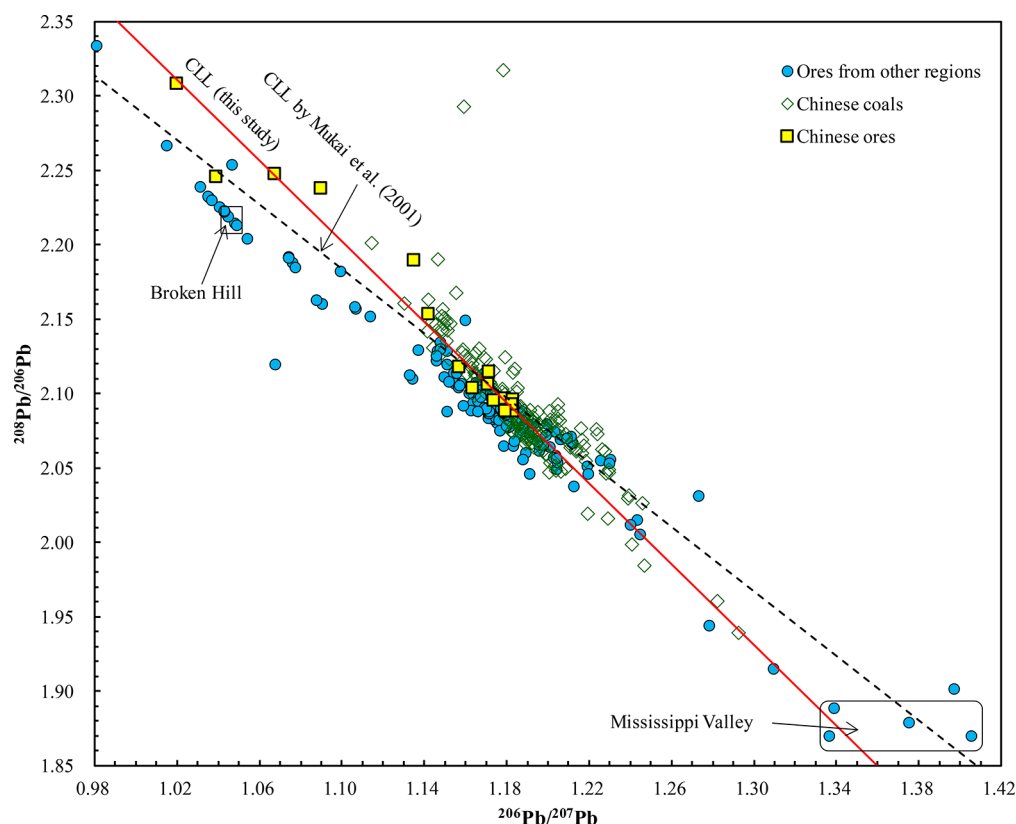


Figure 2. Diagram of $^{206}\text{Pb}/^{207}\text{Pb}$ vs $^{208}\text{Pb}/^{206}\text{Pb}$ in ores from China (data from SI Table S3) and other regions of the world.^{29,30}

become more radiogenic from Northeast to Southwest, which might be explained by the different geotectonic settings of the coal mines. Southwestern China lies in an important mineralization belt with frequent igneous activities carrying radiogenic materials into the coal mines through hydrothermal fluids.^{25,26} On the contrary, North China is a stable Craton platform lack of obvious geological activities, therefore, the coals formed in this region showed a low radiogenic feature.²⁶ Based on the annual coal production (since 1980) of each geographical region, the weighting averages of Pb isotopic compositions in coals were in 1.178–1.182 for $^{206}\text{Pb}/^{207}\text{Pb}$ and in 2.099–2.106 for $^{208}\text{Pb}/^{206}\text{Pb}$ (SI Figure S3), more radiogenic than the previous results ($^{206}\text{Pb}/^{207}\text{Pb}$: 1.176 and $^{208}\text{Pb}/^{206}\text{Pb}$: 2.115).^{18,19,27} It was noted that the average coal radiogenic Pb progressively increased since 1980 (except for the period of 1999–2003) (SI Figure S3). This suggested that bulk coal Pb emissions might become more radiogenic as a result of the change in coal production at each region of China.

There are four important coal-forming periods in China: Late Carboniferous–Early Permian ($\text{C}_3\text{--P}_1$), Late Permian (P_2), Early Jurassic – Middle Jurassic (J_{1-2}), and Late Jurassic – Early Cretaceous ($\text{J}_3\text{--K}_1$). We found that radiogenic Pb in coals would not decrease with their geological ages. Rather, a reverse tendency was observed if removing the samples from $\text{C}_3\text{--P}_1$ (SI Figure S4). This suggested that mixing origins of Pb during and after the coal formation and heterogeneous Th/U distributions could jointly affect the Pb isotopic compositions of coals (especially those from P_2). This agrees with Díaz-Somoano's (2009)⁵ that the generation of heterogeneous Pb isotopic compositions in coals was not monocausal.

Globally, $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios in coals could fit in a same linear regression (Figure 1), suggesting that the

distribution of Pb isotopes in all the world's coals may follow a similar evolution model.²⁸ One-Way ANOVA analysis showed significant differences ($p < 0.01$) in ratios of $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ in coals in China from those in America, but not from those in Europe, Oceania, and South Asia. This implied that coals from the entire Eurasia had a similar isotopic composition, inconsistent with a previous study stating that European coals were statistically more radiogenic than Asian coals.⁵

3.2. Isotopic Composition of Pb in Pb/Zn Ores. Lead isotopic compositions of sphalerite/galena from 16 major Pb/Zn polymetallic deposits in China are presented in SI Table S3 and Figure 2. In comparison with coals, Pb/Zn ores exhibited less radiogenic Pb with $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ in 1.020–1.183 and 2.088–2.309, respectively. Geographically, Pb/Zn deposits from North China (Jiashengpan, Dongshengmiao, Bajiazi, and Caijiaying) had distinctively lower radiogenic Pb ($^{206}\text{Pb}/^{207}\text{Pb} < 1.10$), whereas, the deposits from South China were more radiogenic ($^{206}\text{Pb}/^{207}\text{Pb} > 1.14$), which is consistent with those of the coals. In the diagram of $^{206}\text{Pb}/^{207}\text{Pb}$ vs $^{208}\text{Pb}/^{206}\text{Pb}$, plots of Pb/Zn ores and coals in China fit in a linear regression model (Figure 2), which could be regarded as Chinese lead line (CLL). A previous study reported a similar CLL but with a different slope (Figure 2).²⁹ With more robust data, the CLL in this study would be more representative than the previous one. It is reported that Pb pollution from China (mainly from coal combustion and smelting activities) is characterized by a higher $^{208}\text{Pb}/^{206}\text{Pb}$ signature at a given $^{206}\text{Pb}/^{207}\text{Pb}$ ratio than those from other regions.^{11–13} However, this study showed that Pb/Zn ores from other regions of the world had isotopic compositions close to the CLL (Figure 2), except for those with low radiogenic Pb ($^{206}\text{Pb}/^{207}\text{Pb} < 1.11$)

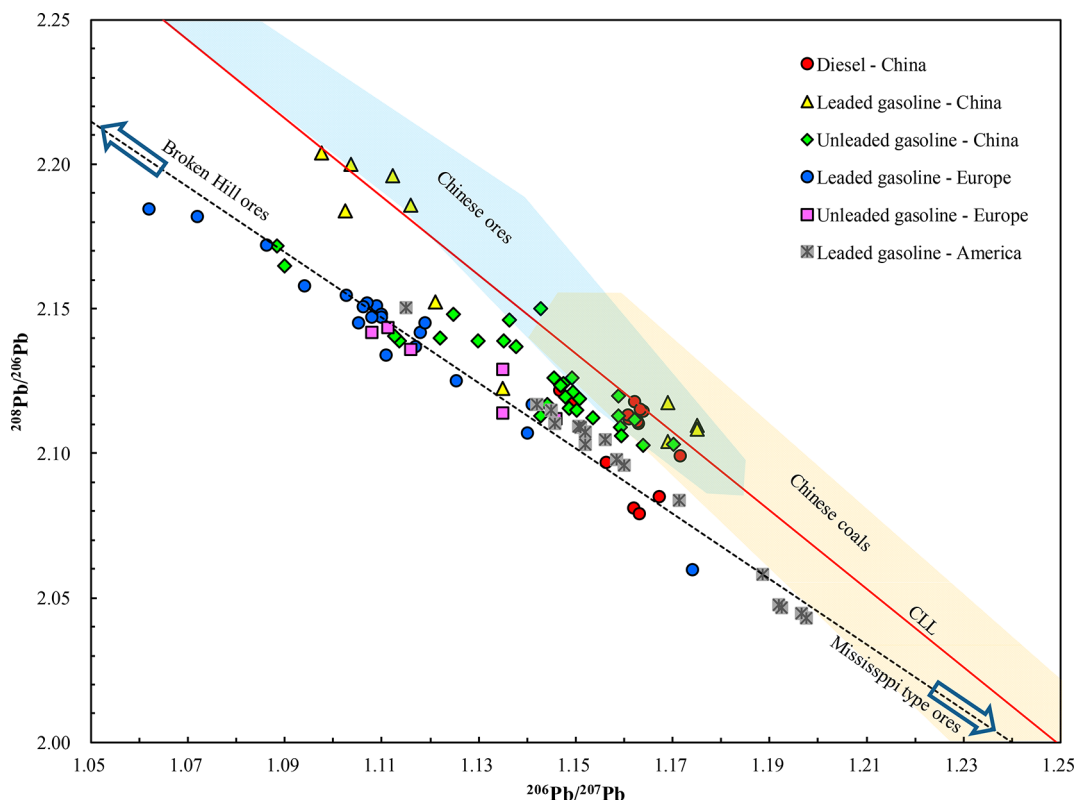


Figure 3. Diagram of $^{206}\text{Pb}/^{207}\text{Pb}$ vs $^{208}\text{Pb}/^{206}\text{Pb}$ in fuels from China (data from SI Table S3), Europe^{31–33} and North America.^{34,35}

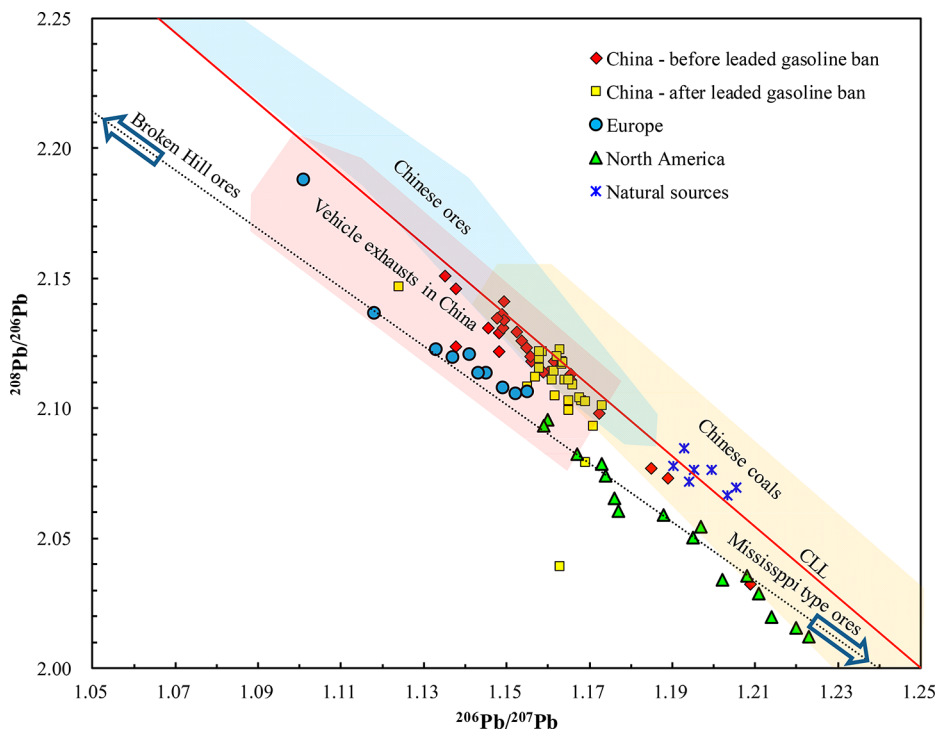


Figure 4. Diagram of $^{206}\text{Pb}/^{207}\text{Pb}$ vs $^{208}\text{Pb}/^{206}\text{Pb}$ in aerosols from China (data from SI Table S4), Europe and North America.^{11,41}

(including Broken Hill ores from Australia). Furthermore, no significant difference ($p > 0.05$) was found for $^{208}\text{Pb}/^{206}\text{Pb}$ ratios in Pb/Zn ores between China and other regions. Therefore, the ores in China were not different in Pb isotopic compositions from those in other regions.

3.3. Isotopic Composition of Pb in Fuels. The Pb isotopic compositions in the fuels ranged from 1.089 to 1.175 for $^{206}\text{Pb}/^{207}\text{Pb}$ and from 2.079 to 2.204 for $^{208}\text{Pb}/^{206}\text{Pb}$ (SI Table S3 and Figure 3). The Pb isotopic ratios of leaded gasoline were controlled by the isotopic compositions of ores, from which the Pb additives for gasoline (alkyllead) were

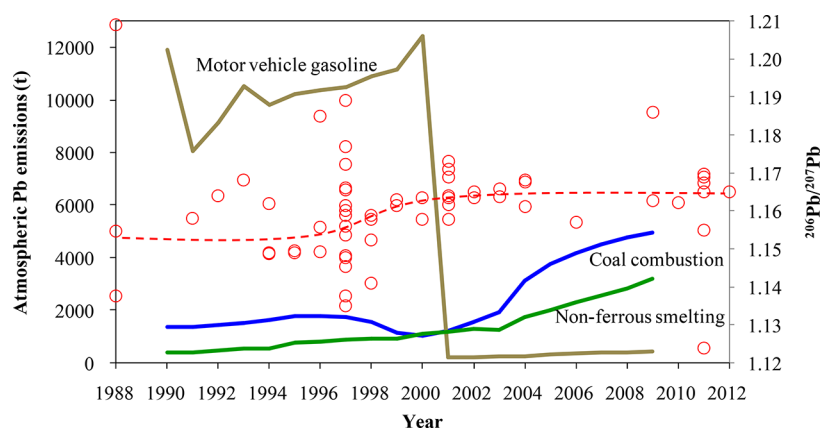


Figure 5. Temporal variation of $^{206}\text{Pb}/^{207}\text{Pb}$ in urban aerosols from China (data from SI Table S4) and atmospheric Pb emission inventories of coal combustion, motor vehicle gasoline combustion, and nonferrous metal smelting.²

produced. Main alkyllead producers included Associated Octel (U.K.) and Ethyl Co. (U.S.).¹¹ The former utilized ores mainly from the Precambrian Broken Hill ore deposits, Australia, which could be characterized by significantly low radiogenic Pb compositions ($^{206}\text{Pb}/^{207}\text{Pb} = 1.0407$, $^{208}\text{Pb}/^{206}\text{Pb} = 2.2248$).³⁰ The later utilized ores from Mississippi Valley with an anomalously high $^{206}\text{Pb}/^{207}\text{Pb}$ ratio (~ 1.134).³⁰ In China, Pb additives imported from Associated Octel had been used since 1990.¹⁸ However, the Pb isotopic ratios in most leaded gasoline from China were consistent with those of the native Pb/Zn ores, but different from the Broken Hill ores or European gasoline, neither the Mississippi type ores or American gasoline. This suggested that Pb additives used in China were mainly from domestic ores.

Since alkyllead was completely prohibited to use in 2000, concentrations of Pb in gasoline decreased significantly. However, the unleaded gasoline in China still contained a small amount of Pb (60–280 $\mu\text{g}/\text{L}$), which is inherited from the crude oils.^{36–38} In this study, a wide range of Pb concentrations (8–450 mg/kg) in the soots from unleaded gasoline exhaust pipes were detected, lower than those from leaded gasoline (7804 ± 160 mg/kg), but its contribution to the atmospheric Pb should not be completely ruled out. Unlike the leaded gasoline, the unleaded gasoline had lower ratios of $^{208}\text{Pb}/^{206}\text{Pb}$ at a given $^{206}\text{Pb}/^{207}\text{Pb}$ value, shifting toward the European and American gasoline, suggesting the mixing of both domestic and alien sources. This was consistent with the fact that more than half of the market gasoline in China were imported during the past decade.⁶

Generally, the diesel is richer in Pb (~ 2000 $\mu\text{g}/\text{L}$) than unleaded gasoline.³⁹ In this study, a much higher Pb concentration (4072 mg/kg) was observed in diesel soot than in unleaded gasoline soots (SI Table S3). Since the consumption of diesel is about twice that of gasoline in China, the emission of Pb to the atmosphere from diesel would be more pronounced than from unleaded gasoline. It is observed that the diesel Pb isotopic compositions were more radiogenic than those of the unleaded gasoline in China (at significant difference of $p < 0.01$). Nevertheless, some diesel samples showed a mixing feature of Pb isotopic compositions, similar to the unleaded gasoline in China.

Due to the complexity of fuels used in China, it is difficult to successfully conduct the source tracing merely dependent on Pb isotopic compositions. However, the average Pb isotopic ratios of fuels (both domestic and abroad) were significantly

different ($p < 0.01$) from those of coals in China, leading to the possibility to discriminate Pb in fuels from in coals.

3.4. Isotopic Composition of Pb in Aerosols. Aerosol is regarded as an effective indicator to monitor real time atmospheric pollution. Ratios of $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ in aerosols from main cities in China are presented in SI Table S4 and Figure 4. In general, Pb in the aerosol samples was less radiogenic than those from natural sources, indicating evident anthropogenic contributions. Ratios of $^{208}\text{Pb}/^{206}\text{Pb}$ in aerosols from China were higher at a given $^{206}\text{Pb}/^{207}\text{Pb}$ value than those from Europe and North America, and were plotted along the CLL (Figure 4), suggesting the dominance of domestic Pb in the aerosols. However, the isotopic signatures of the aerosols slightly shifted toward the gasoline domain, indicating a possible contribution of vehicle exhausts. After removing the leaded gasoline since 1998, the levels of Pb in aerosols from China showed a significantly declining tendency (average value was decreased from 286 ng/m^3 to 188 ng/m^3) (SI Table S4), but still much higher than those from European and North American (< 20 ng/m^3).¹¹ This can be supported by the increasing emissions of Pb from coal combustion and other industrial activities, especially from nonferrous metal smelting in China (Figure 5). Nevertheless, the aerosol Pb in China became more radiogenic after removing the leaded gasoline (Figures 4 and 5), which is related to the increasing contribution to atmospheric Pb from coals (increased from 9.8% in 1990 to 51.6% in 2009).² However, such temporal evolution was inconsistent among the four regions in China (Figure 6). Aerosols from Tianjin (North China) and Shanghai (East China) showed an increment in radiogenic Pb after removing the leaded gasoline.^{2,27} While a reverse trend for Pb isotope evolution in aerosols from Guiyang (Southwestern China) was observed, which varied from coal-domination before leaded gasoline ban to fuel-domination after removing the leaded gasoline. This may be explained by the facts that (i) coal was the most important source of atmospheric Pb pollution in Guiyang before leaded gasoline ban due to a limited amount of motor vehicles at that time,^{25,41} and (ii) fuel combustion emissions (from unleaded gasoline and diesel) have now become the major source of atmospheric Pb in Guiyang due to the exponential increase in vehicles after elimination of coal boilers during the past decades.⁴¹ As for Guangdong (South China), the Pb isotopic signatures in aerosols remained similar before and after the leaded gasoline ban. This may be explained by the following facts: (i) in

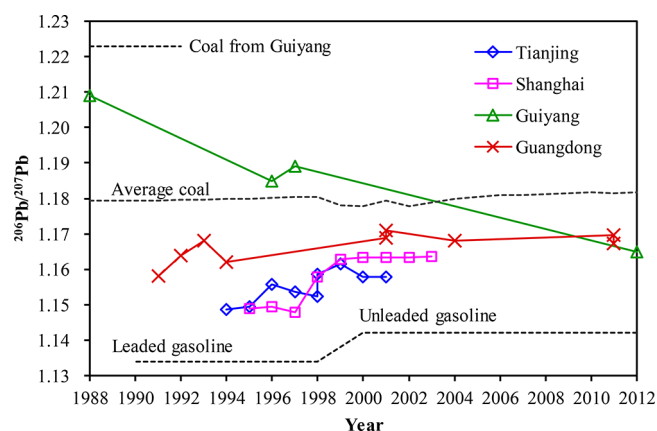


Figure 6. Temporal variation of $^{206}\text{Pb}/^{207}\text{Pb}$ in aerosols from Tianjin, Shanghai, and Guiyang cities and Guangdong province (data from SI Table S4). The data of coals from Guiyang, leaded gasoline and unleaded gasoline are from SI Table S4, the data of average coal (1990–2012) are from SI Figure S3.

Guangdong, vehicle emissions have always been a major atmospheric Pb source due to the heavy traffic;^{2,41} and (ii) Pb additives, historically used in Guangdong, were generated from local ores, which had a similar isotopic composition to the coals (Figure 2).

This study provides a full data set for Pb isotopic compositions in coals, fuels, and Pb/Zn ores from China, which might be useful for tracing Pb pollution at both regional and global scales. However, it remains a big challenge for Pb pollution tracing in China, due to the complexity of Pb isotopic compositions in various sources, regional variation of Pb sources, and the similarity of Pb isotopic compositions among sources (e.g., coals, ores, and fuels, and foreign sources). This can also be enhanced by the Chinese situation in the near future because (i) the Chinese government has started extensive campaigns to eliminate high-energy consumption and heavy-pollution industries. For example, electrostatic precipitator (ESP) and flue gas desulfurization (FGD) with a Pb removal efficiency up to 97% have been installed for most coal-fired boilers (>95%) in China;^{20,42} (ii) clean energy, such as natural gas, electrical, solar and wind energy, has been widely adopted to replace coal usage, even though the current consumption of coals is still high;⁶ and (iii) contributions from new emerging pollution sources (e.g., cement and electronic waste) and alien Pb (coal, petroleum, natural gas, metallic materials, etc.) have increased their significance.^{2,6,14,43–45} Therefore, it is of great importance to maintain the monitoring of Pb isotopic compositions from emerging anthropogenic sources and to offer updated data set.⁴⁰

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.7b04119.

Figures S1–S4 and Tables S1–S4 (PDF)

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Notes

The authors declare no competing financial interest.

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