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Atmospheric lead in urban Guiyang, Southwest China: Isotopic source signatures

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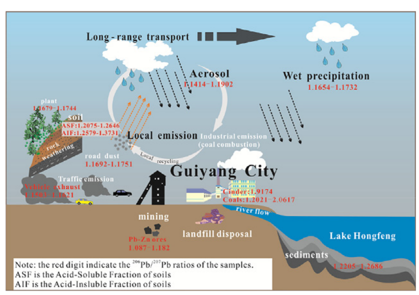
HIGHLIGHTS

- The coals from Guizhou province had abnormally high radiogenic Pb.
- Coal combustion was not the major source of atmospheric Pb in Guiyang area.
- Atmospheric Pb mainly originated from industrial emission or vehicle exhaust.

GRAPHICAL ABSTRACT



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ABSTRACT

Total suspended particles (TSP) and their source-related samples from Guiyang, Southwest China, were collected and analyzed for their lead (Pb) concentrations and Pb isotopic compositions, to identify the sources of atmosphere lead in urban Guiyang. Coals from Guizhou Province had significantly high radiogenic Pb, different to those from North China. Local vehicle exhaust had similar Pb isotope ratios to those of other areas in China. Pb isotopic compositions of atmospheric aerosols, rainwaters, plant samples, and acid-soluble fraction of street dusts were similar to each other. The results clearly suggest that the Pb–Zn ore-related industrial emission, and/or vehicle exhaust, rather than the local coal combustion, are the main sources of atmospheric Pb in Guiyang. Furthermore, binary mixing model indicates that the contribution of coal combustion to the local atmospheric Pb decreased from about 40% in 1988 to about 10% in 2013.

1. Introduction

Atmospheric lead (Pb) pollution is a global problem owing to its detrimental effects on not only human health but also the natural ecosystem. Researches have increasingly focused on the pollution

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sources and atmospheric transport of Pb (Chiaradia et al., 1997; Sturges and Barrie, 1987; Weiss et al., 1999; Flament et al., 2002; Widory et al., 2004). Anthropogenic Pb pollution originates mainly from mining, smelting, industrial uses, waste incineration, coal combustion, and leaded gasoline (Cheng and Hu, 2010). The atmospheric levels of Pb increases significantly since the use of alkyl lead as an antiknock agent in combustion engines in 1920s. Thus, vehicle emission, especially the leaded gasoline combustion, is generally considered as one of the dominant sources of atmospheric Pb pollution. From the mid-1970s, atmospheric Pb levels have decreased in some western cities due to the phasing out of leaded gasoline (Widory et al., 2004; Hinrichs et al., 2002). Besides vehicle exhaust, other sources, such as industrial emission, coal combustion and refuse incineration also contribute to atmospheric Pb pollution (Mukai et al., 1993, 1994; 2001; Xu et al., 2012; Sturges and Barrie, 1989).

Lead has four naturally stable isotopes (^{204}Pb, ^{206}Pb, ^{207}Pb, and ^{208}Pb). Due to the small fractional mass differences among these isotopes, ordinary chemical, physical or biological reactions cannot obviously influence the isotopic composition of Pb. Consequently, Pb isotope has been used as a fingerprint for tracing its sources and transport in the environment. Bollhöfer and Rosman (2000, 2001) investigated the global isotopic signature of atmospheric Pb using its isotope ratios. Studies of airborne particulate matter from Asian cities demonstrated that atmospheric Pb levels in urban China were considerably influenced by coal combustion and industrial emission, despite the usage of leaded gasoline (Mukai et al., 1993, 2001). Since the banning of leaded gasoline in China in the year of 2000 (Wang et al., 2006), many studies have been conducted to investigate the main sources of atmospheric Pb in Chinese megacities such as Shanghai (Zheng et al., 2004; Chen et al., 2005; Li et al., 2009), Tianjin (Wang et al., 2006.), as well as the Pearl River Delta region (Wong et al., 2003; Lee et al., 2005; Zhu et al., 2001) including Guangzhou (Duzgoren-Aydin, 2007) and Hong Kong (Duzgoren-Aydin et al., 2004; Lee et al., 2006). In the past decade, due to the policy of the China Western Development that is to boost the economy in the less developed regions, some studies focused on environmental problems such as Pb pollution in urban and remote regions in the western China such as Chengdu (Gao et al., 2004.), Xi'an (Xu et al., 2012), Waliguan (Cheng et al., 2007) and Lhasa (Cong et al., 2011).

Guiyang is the capital of Guizhou Province, which is one of the largest coal producing provinces in China. It is an important industrial base for electricity and ferric, steel, and phosphorus, and is considered as one of the most seriously polluted cities in southwestern China. A recent study demonstrated that atmospheric input is one of two main sources of Pb in vegetables of Guiyang (Li et al., 2012). Coal combustion was suggested to be the major source of atmospheric Pb in Guiyang (Mukai et al., 1993, 2001). However, such a conclusion was based on the Pb isotopic ratios of coal samples from North China (Mukai et al., 2001), not from the local region. In fact, the Pb isotopic compositions of coal samples varied from one site to another worldwidely (Díaz-Somoano et al., 2009). Pb isotope ratios of rocks in South China have also been proven to be different from those in North China (Zhu, 1995). Thus, similar to their difference in sulfur isotope ratios (−3‰ vs. +5‰) (Mukai et al., 2001; Liu et al., 1996), Pb isotopic compositions of coal samples in Guizhou province may also be different from those in North China.

In this study, total suspended particle (TSP) samples, together with rainwater, street dust, soil and lake sediments, moss and plant leaf samples, as well as vehicle exhaust and coal samples were collected from Guiyang, China. Their Pb concentrations and isotope ratios were analyzed to provide a comprehensive view of Pb in different environmental samples, which help to better understand their potential contributions to atmospheric Pb in Guiyang.

2. Materials and methods

2.1. Sampling

In order to study the isotopic composition of atmospheric Pb, environmental samples, including ten rainwater samples, 8 TSP samples, 8 street dust samples, 8 plant samples, the potential sources, including 4 vehicle exhaust samples, 15 coal samples and one cinder in power plant, as well as 7 soils and 33 lake sediments were collected from Guiyang area. The information of sampling method was listed in detail in supporting information and sampling sites was shown in Fig. 1.

2.2. Analytical methods

Coal and cinder samples were crushed in a carnelian bowl. After the dryness at 45 °C, soils, sediments and street dusts were sieved through a 2-mm plastic sieve to remove large debris, gravel-size materials, plant roots and other waste materials. Then, they were homogenized and ground with an agate mortar and kept in a desiccator. Plant leaf and the green part of moss (top 1–2 cm)

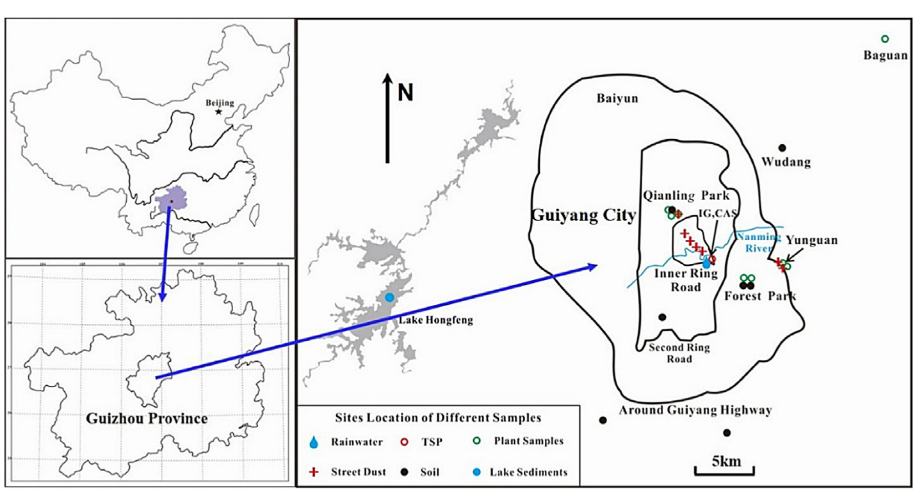

Fig. 1. A map showing the sampling sites in Guiyang, China.

samples were washed in deionized (DI) water to wipe off the soil particles, dried at 60 °C, crushed and ashed at temperature of 450 °C, and then dissolved in HNO_3 (with a few drops of HF solution). Rainwater samples were dried at 75 °C before separation. One quarter of each TSP filter sample was cut using stainless steel scissors and digested by a mixture of concentrated HNO_3 and HF in acid-cleaned PFA beaker (Savillex). In this study, only the acid soluble fraction (extracted by 4% HNO_3) of street dusts was extracted for analysis, because the acid extraction method can separate polluted Pb from geogenic Pb (Zhu et al., 2001; Gioia et al., 2006; Outridge et al., 2002). Soil and lake sediment samples were separated into acid-soluble fraction (extracted by 4% HNO_3) and acid-insoluble fraction (dissolved in HNO_3 and HF). The data of acid-soluble fraction of the lake sediment samples were reported previously (Zhao et al., 2011). The acid-insoluble fraction of soils and sediments were taken as the representative of regional background level in Guiyang area.

Lead isotope measurement was performed by the separation using a micro exchange column with Dowex-1 × 8 (200–400 mesh) anion resin with HBr and HCl as eluents (Zhu et al., 2001). The chemical separation processes were performed in a clean room. All acids were purified by double distillation. The total Pb blank for the procedure was lower than 100 pg.

The Pb concentrations (and U concentrations of coal samples) were measured by an inductively coupled plasma mass spectrometer (ICP-MS, Micro mass, Platform), with its precision better than 10%. The Pb isotopic compositions were measured by a multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS, Nu Instruments Ltd., Nu Plasma). Pb isotope ratios were corrected using the $^{203}Tl/^{205}Tl$ ratio with an exponential law function (Belshaw et al., 1998). During the experiment, the values measured for the standard NIST SRM-981 were $^{206}Pb/^{204}Pb = 16.937 \pm 0.005$ (2σ), $^{207}Pb/^{204}Pb = 15.492 \pm 0.006$ (2σ), $^{208}Pb/^{204}Pb = 36.702 \pm 0.020$ (2σ), $^{208}Pb/^{206}Pb = 2.16689 \pm 0.00063$ (2σ), and $^{207}Pb/^{206}Pb = 0.91465 \pm 0.00012$ (2σ), which agree with the recalibrated values of 16.9405, 15.4963, 36.7219, 2.16771, and 0.914750, respectively (Galer and Abouchami, 1998).

3. Results

The Pb concentrations and Pb isotope ratios for the samples measured in this study are listed in Table S1 with their detailed information in Table S2. The acid-soluble fraction of street dust samples showed the highest Pb concentration among all samples except TSP, ranging from 86.3 to 412.5 mg/kg, which were lower than those in street dusts from Hong Kong (327 ± 54 mg/kg) (Duzgoren-Aydin et al., 2004). Lead concentrations of the TSP samples varied from 6.9 to 591.3 ng/m^3, which were similar to the annual average value of Xi'an (306 ng/m^3) (Xu et al., 2012), but were higher than the average value of aerosols from Xiamen (79.1 ± 38.3 ng/m^3) (Zhu et al., 2010). Pb concentration in the particulate matter (TSP) varied in the range of 546–3989 mg/kg. Plant leaf and moss samples showed Pb concentrations in the range of 2.2–75.4 mg/kg, which were lower than those in mosses from Nanling (averaged on 69.3–296 mg/kg) (Lee et al., 2005). The Pb concentrations of vehicle exhaust varied from 17.6 to 39.7 mg/kg. The acid-soluble fraction of soils had Pb concentrations (21.9–77.8 mg/kg) generally higher than those (19.7–25.9 mg/kg) of the acid-insoluble fraction. Coal samples had Pb concentrations between 0.9 and 35.2 mg/kg.

According to the Pb isotopic compositions, the samples studied here can be roughly clustered into three groups. The first group, including TSP, rainwater, vehicle exhaust, plant samples, and the acid-soluble fraction of street dust samples, is characterized by the lowest $^{206}Pb/^{207}Pb$ ratio (1.1414–1.1902) and the highest $^{208}Pb/^{206}Pb$ ratio (2.0591–2.1298). The second group, represented by the coal samples from Guizhou Province, is characterized by the highest radiogenic Pb, with isotope ratios of 1.2021–2.0617 for $^{206}Pb/^{207}Pb$ and 1.1610–2.0834 for $^{208}Pb/^{206}Pb$. The third group, including the soils and lake sediments (acid-insoluble fraction), has middle $^{206}Pb/^{207}Pb$ (1.2205–1.2787) and $^{208}Pb/^{206}Pb$ ratios (1.9428–2.0292). The acid-soluble fraction of soils had a larger-scale isotopic variation ($^{206}Pb/^{207}Pb$: 1.2075–1.2917; $^{208}Pb/^{206}Pb$: 1.9031–2.0435) than the acid-insoluble fraction.

4. Discussions

4.1. Lead isotope ratios of natural background samples in Guiyang

The natural background characteristics of Pb isotopic signatures in rocks and soils are necessary to understand the sources of Pb pollution. The Pb isotope mapping result of China demonstrated that Pb isotope ratios varied among different geological blocks, in which Guizhou province is belong to the Yangtze Block (Zhu, 1995). The published isotope ratios for Pb–Zn ore samples from Guizhou Province (Wang, 1993) (Fig. 2) may not represent the background signature of Guiyang area. Rather, it may be an anthropogenic source of atmospheric Pb pollution, because a lot of Pb–Zn ores in Guizhou have already been exploited as important mineral resource which would cause Pb pollution to the surroundings.

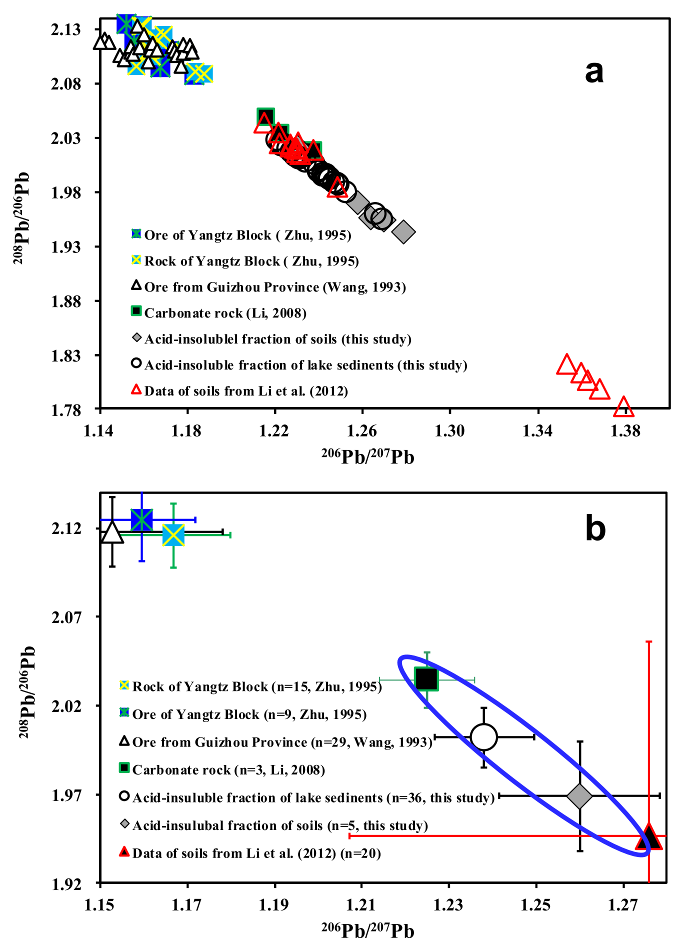

Fig. 2. Lead isotopic composition of the background samples from Guiyang area. All related samples were plotted in (a) and their average values were summarized in (b). The error bars indicate the values of 1SD. The oval-shaped area illustrates the background Pb isotopes in Guiyang area.

The reported data of rock samples in Guiyang area is limited. Pb isotope ratios (1.2156–1.2370 for $^{206}Pb/^{207}Pb$ and 2.0191–2.0499 for $^{208}Pb/^{206}Pb$) of three carbonate rocks from Guiyang area were measured recently (Li, 2008).

The Pb isotope ratios of soils should be a mixture of the regional background signature and anthropogenic input. Lake sediments are recognized to provide a record of the natural and anthropogenic inputs of contaminants into the basin-scale environment. The Pb isotope ratios of the acid-insoluble fraction of the soils in this study varied in the range of 1.2300–1.2787 for $^{206}Pb/^{207}Pb$ and 1.9428–2.0211 for $^{208}Pb/^{206}Pb$, with similar average values (1.2600 ± 0.0184 and 1.9690 ± 0.0307, respectively) to the recently reported data of soils from suburban area of Guiyang (1.276 ± 0.07 and 1.947 ± 0.11) (Li et al., 2012) (Fig. 2). The average Pb isotope ratios the acid-insoluble fraction of sediments from Lake Hongfeng were 1.2381 ± 0.0115 for $^{206}Pb/^{207}Pb$ and 2.0020 ± 0.0169 for $^{208}Pb/^{206}Pb$ (Fig. 2). So, it is reasonable to roughly restrict the regional background Pb isotope ratios in the ranges of 1.22–1.28 for $^{206}Pb/^{207}Pb$ and 1.95–2.03 for $^{208}Pb/^{206}Pb$. According to the previous studies (Zhu et al., 2001; Gioia et al., 2006; Outridge et al., 2002), the acid-insoluble fraction of soils and lake sediments studied here should be the representative of the regional background.

4.2. Pb isotope ratios of local coal samples

As coal is a potential anthropogenic source of atmospheric Pb, its Pb concentration and Pb isotope ratio are of great interest. However, few Pb isotope data for Chinese coals have been published. $^{206}Pb/^{207}Pb$ ratios of some Chinese coals were reported to be 1.14–1.22 (Mukai et al., 1993). The $^{206}Pb/^{207}Pb$ ratios of coals used in Shanghai were reported to range from 1.140 to 1.208 (Zheng et al., 2004; Chen et al., 2005). These studies were focused on the coals from North China. The three North China coals examined in the present study have $^{206}Pb/^{207}Pb$ ratios in the range of 1.1841–1.1945, and $^{208}Pb/^{206}Pb$ ratios of 2.0646–2.0850. In comparison, the 12 coals from Guizhou Province have average $^{206}Pb/^{207}Pb$ ratio of 1.4140 and average $^{208}Pb/^{206}Pb$ ratio of 1.8146. The cinder sample had $^{206}Pb/^{207}Pb$ ratio of 1.2951 and $^{208}Pb/^{206}Pb$ ratio of 1.9174, approximately similar to the average values of the 12 coal samples from Guizhou Province, but clearly different to those of the coals from North China, which implies that coals consumed in Guiyang area are mainly from Guizhou Province.

In a isotopic composition plot for Pb (Fig. 3), most of the North China coals fall into a small area (highlighted by a blue oval). In comparison, coals from Guizhou Province have a greater scattering of $^{208}Pb/^{206}Pb$ and $^{206}Pb/^{207}Pb$ ratios, similar to the high-uranium (U) coals from the Czech Republic (Mihaljevič et al., 2009). The labeled numerical values in Fig. 3 are the U/Pb mass ratios of the corresponding samples. $^{206}Pb/^{207}Pb$ ratios of coal samples from Guizhou Province and the high-uranium coals from the Czech Republic are positively correlated to their U/Pb ratios (Fig. 3). The higher $^{206}Pb/^{207}Pb$ ratios of the high-uranium coals are attributed to mixing of the isotope ratios of common Pb in organic material at the time of sedimentation and radioactive products of the subsequently transported U (Mihaljevič et al., 2009). Relatively high U contents have been observed in coals from some coalfields in western Guizhou Province, and were attributed to the influence of thermal liquid after coal sedimentation and terrestrial clastic matter (Dai et al., 2004). Therefore, the abnormally high radiogenic Pb isotopic composition of the Guizhou coal was a result of mixing of the isotope ratios of common Pb in organic material, the radioactive products of U from terrestrial material, and the radioactive products of the subsequently transported U.

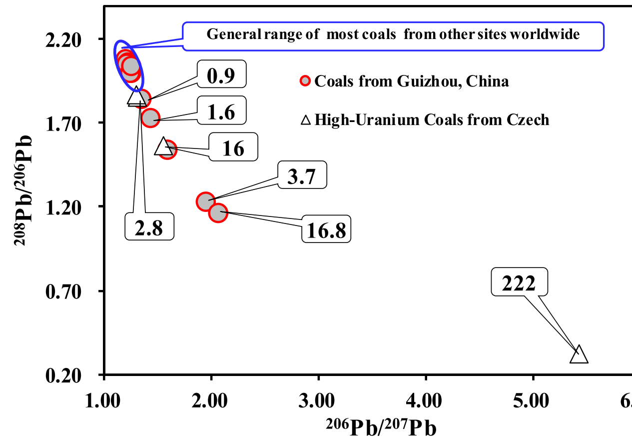

Fig. 3. Comparison of Pb isotope ratios of coal samples from Guizhou Province and from other sites worldwide. Most of the previous reported data falls within the area highlighted by the blue oval. Coals from Guizhou Province and high-uranium coals from Czech Republic (Mihaljevič et al., 2009) are characterized by abnormally high radiogenic Pb. The labeled numerical values are the U/Pb mass ratios of the corresponding samples. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

4.3. Pb isotope ratios of traffic pollutant

Petrol with alkyl-lead additives was historically a major source of Pb pollution. These additives can be distinguished by their Pb isotopic compositions. Alkyl-lead additive from Ethyl Corp. (US) has high $^{206}Pb/^{207}Pb$ (1.225 ± 0.005) and low $^{208}Pb/^{206}Pb$ (2.012 ± 0.005) ratios (Sturges and Barrie, 1989). In contrast, alkyl-lead additive from Associated Octel Co. Ltd. (UK) has low $^{206}Pb/^{207}Pb$ (1.055 ± 0.005) and high $^{208}Pb/^{206}Pb$ (2.213 ± 0.005) ratios (Bollhöfer and Rosman, 2000).

There are only a few studies of Pb isotopic compositions for Chinese gasoline and vehicle exhaust (Zhu et al., 2003). In a three-isotope plot for Pb, the Pb isotope ratios for vehicle exhaust samples in this study were similar to those reported for Chengdu and Guangzhou, characterized by binary mixing of US-type and UK-type Pb-additives (Figure S1). This indicates that the lead in fuel used in China have similar origins. Due to the sampling period, it also suggests that the isotopic compositions of vehicle exhaust did not change notably before and after the phasing out of leaded petrol in these cities, different from the obvious change in Shanghai (Chen et al., 2005).

4.4. Pb isotope ratios of atmospheric aerosols and other environmental samples in Guiyang

Atmospheric Pb is considered to be present in fine aerosol particles that can be transproted over long distances (Komárek et al., 2008). Thus, the long-range transported atmospheric Pb is not negligible. For example, studies have shown that Pb isotopic composition in European aerosols could be influenced by Pb in the Saharan dust aerosols (Doucet and Carignan, 2011). However, Guiyang city is located in a basin region surrounded by mountains, which may indicate that the local emitted Pb should be more significant than those from long-range atmospheric transport.

The $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ ratios of the TSP, rainwater, plant, and the acid-soluble fraction of street dust samples are plotted in Fig. 4. Although the Pb isotopic ratios of TSP varied a wider range than those of rainwater, plant and street dust samples, their average values were similar, which indicate a similar Pb source. Previously reported data of rainwater samples from Guiyang (Li et al., 2012) were also similar to those of the present

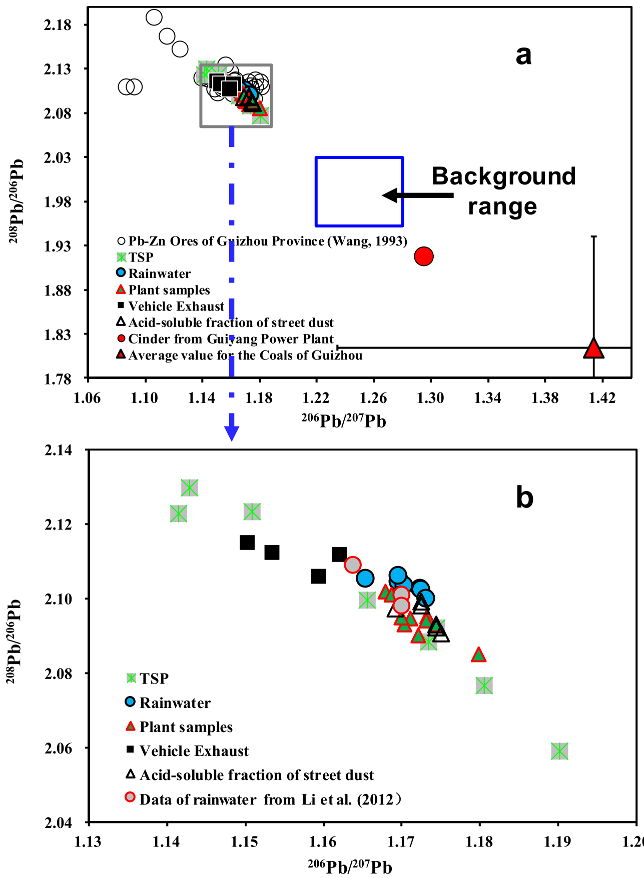

Fig. 4. Lead isotopic compositions of the environmental samples from Guiyang, China. Data of local vehicle exhaust samples and coal samples, Pb–Zn ore samples from Guizhou Province (Wang, 1993), as well as the range of regional background we assigned for Guiyang area were also included in (a) for comparison. All data in the small gray rectangle of (a) are enlarged to (b). The error bars indicate the values of 1SD.

study (Fig. 4b). All these samples are isotopically close to the vehicle exhaust samples and the Pb–Zn ore samples from Guizhou Province, but clearly different from the local coal samples. This implies that the TSP, plant, rainwater, and street dust samples have been polluted most probably by gasoline Pb or local Pb-bearing ores.

Furthermore, coal samples and the cinder sample are all characterized by higher radiogenic Pb compared with the local background. This indicates that, at least for the period of our sampling, coal combustion should not be a major source of atmospheric Pb pollution in Guiyang. Previous researches concluded that the difference of Pb isotope ratios of particulate matter between Guiyang and North China cities was attributed to the higher contribution of coal combustion in Guiyang than in other cities (Mukai et al., 1993). However, based on these considerations about both Pb isotopic signature in background soil and coal, the contribution of coal to Pb pollution in Guiyang should be evaluated to be lower than those expected previously.

Our results show that the Pb isotopic compositions of Guizhou coals are clearly different from North China coals. It is also necessary to emphasize that the local background message of Pb in Guiyang is likely to be different from those in other parts of China. The relatively greater variation of the acid-soluble fraction for the soils than those of the acid-insoluble fraction should be attributed to the historical accumulation result of the atmospheric Pb in this region, and the evolution of the major Pb pollution sources in this region.

4.5. Long-term evolution of atmospheric Pb isotope ratios in Guiyang

To determine whether the Pb pollution sources have been changed since the 1980s to present day, we compared the results of our TSP and street dust samples with the reported data of airborne particulate in 1980s (Mukai et al., 1993, 2001) (Fig. 5a). Data of the rainwater samples are also included for comparing. The averaged $^{206}Pb/^{207}Pb$ ratio of atmospheric matter decreased continually from 1988 to 2013, with about 1.21 in 1988 and 1.1649 in 2013. Over the same period, the $^{208}Pb/^{206}Pb$ ratios increased from 2.03 (1988) to 2.1047 (2013). Such a temporal trend, continually deviating from the coal-combustion source, highlights that the sources of atmospheric Pb in Guiyang has been changed. The contribution of Pb–Zn ore-related Pb source or/and vehicle exhaust pollution obviously increased in the last two decades, while the contribution of coal combustion continually decreased.

In Fig. 4, the major sources of atmospheric Pb in Guiyang should be a combination of a binary mixing. In addition to coal combustion, other sources should be industrial emission, represented by the local Pb-bearing ores with average ratios of

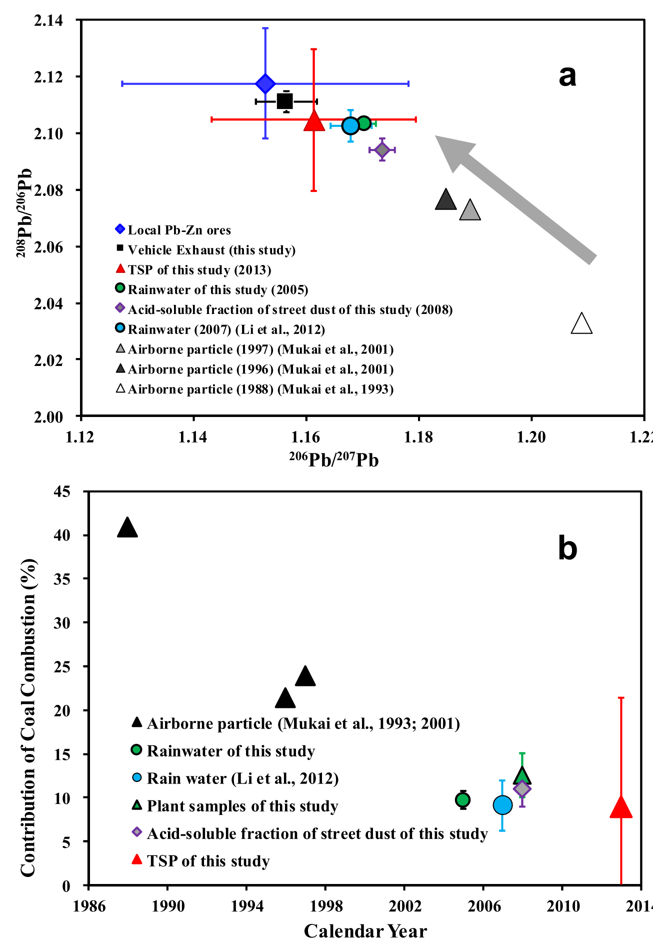

Fig. 5. (a) Comparison of Pb isotope ratios of TSP samples from this study with the previously reported data of airborne particulate matter from Guiyang, China. Local Pb–Zn ores), vehicle exhaust sample, data of rainwater of this study and from Li et al. (2012) are also included for comparison. Numbers in the brackets are the sampling years. The gray arrow indicates the historical evolution trend of Pb isotope ratios in the atmosphere of Guiyang. (b) Long-term evolution of the calculated contribution of coal combustion to atmospheric Pb in Guiyang, see text in detail. The data of plant samples and acid-soluble fraction of street dusts were also included. The error bars indicate the values of 1SD.

$^{206}Pb/^{207}Pb = 1.1527$ and $^{208}Pb/^{206}Pb = 2.1177$ (calculated from Wang, 1993), and/or vehicle exhaust emission. Though the Pb isotope ratios of Guizhou coals vary over a large range, the Pb isotope ratios of the cinder sample from the Guiyang power plant is in the range of the 12 Guizhou coal samples. Therefore, we take the cinder sample ($^{206}Pb/^{207}Pb = 1.2951$, $^{208}Pb/^{206}Pb = 1.9174$) as the end member of coal combustion. Assuming that the Pb in rainwater and airborne particulate matter all originate from pollution, the contributions of the two primary pollution sources to airborne particulate matter and rainwater samples can be calculated using this binary mixing model. The result shows that from 1988 to 2013, the contribution of coal combustion-related pollution source to the atmospheric Pb in Guiyang area clearly decreased from about 40% (1988) to the currently value, about 10% (Fig. 5b). The result for plant sample is also similar to those of rainwater and TSP samples.

If coal combustion was the major atmospheric Pb pollution source, according to the climatic characteristic in Guiyang, with a warm summer and a cold winter, and the characteristic of energy consumption, dominant in coal combustion, coal consumption must be different between the seasons in Guyang. This will result in the variation of contribution from coal combustion for the atmospherical Pb. But the similarity of Pb isotope ratios in rainwater samples collected in different seasons (Table S2) cannot support this hypothesis. So, in contrast, it suggested that industrial emission and/or vehicle exhaust being the major Pb source. Owing to the similar Pb isotopic compositions of these primary sources, it is difficult to distinguish them from each other at this moment, which warrants further studies.

Our results show that the major source of atmospheric Pb in Guiyang area has changed during the past 20 years. Atmospheric Pb in Guiyang should be mainly originated from the industrial and/or vehicle exhaust emissions at the present day. This is different from that of some other Chinese cities, eg. Wuhan (Zhu et al., 2013) and Guangzhou (Bi et al., 2013).

5. Conclusions

Atmospheric aerosols, rainwater, coal and other source-related environmental samples from Guiyang, Southwest China, were collected and analyzed for their Pb concentrations and Pb isotopic compositions. Lead concentrations of the aerosol samples varied from 6.9 to 591.3 ng/m^3. Atmospheric aerosols, rainwater, vehicle exhaust and plant samples were characterized by the lowest $^{206}Pb/^{207}Pb$ ratio (1.1414–1.1902) and the highest $^{208}Pb/^{206}Pb$ ratio (2.0591–2.1298). Coals from local regions in Guizhou Province had significantly high radiogenic Pb, different to those from North China. Our results show that the atmospheric Pb sources of Guiyang area have been clearly changed from 1980s to the present, which were characterized by the decreased contribution from coal combustion and the increased contribution from Pb–Zn ore-related emission and/or vehicle exhaust.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2015.05.049.

References

Bi, X., Liang, S., Li, X., 2013. A novel in situ method for sampling urban soil dust: particle size distribution, trace metal concentrations, and stable lead isotopes. Environ. Pollut. 177, 48–57.
Bollhöfer, A., Rosman, K.J.R., 2000. Isotopic source signatures for atmospheric lead: the Southern Hemisphere. Geochim. Cosmochim. Acta 64, 3251–3262.
Bollhöfer, A., Rosman, K.J.R., 2001. Isotopic source signatures for atmospheric lead: the Northern Hemisphere. Geochim. Cosmochim. Acta 65, 1727–1740.
Belshaw, N.S., Freedman, P.A., O'Nions, R.K., Frank, M., Guo, Y., 1998. A new variable dispersion double-focusing plasma mass spectrometer with performance illustrated for Pb isotopes. Int. J. Mass. Spectrom. 181, 51–58. http://dx.doi.org/10.1016/S0016-7037(02)00955-9.
Chen, J., Tan, M., Li, Y., Zhang, Y., Lu, W., Tong, Y., Zhang, G., Li, Y., 2005. A lead isotope record of shanghai atmospheric lead emissions in total suspended particles during the period of phasing out of leaded gasoline. Atmos. Environ. 39, 1245–1253. http://dx.doi.org/10.1016/j.atmosenv.2004.10.041.
Cheng, H., Hu, Y., 2010. Lead (Pb) isotopic fingerprinting and its applications in lead pollution studies in China: a review. Environ. Pollut. 158, 1134–1146. http://dx.doi.org/10.1016/j.envpol.2009.12.028.
Cheng, H., Zhang, G., Jiang, J.X., Li, X., Liu, X., Li, J., Zhao, Y., 2007. Organochlorine pesticides, polybrominated biphenyl ethers and lead isotopes during the spring time at the Waliguan Baseline Observatory, northwest China: Implication for long-range atmospheric transport. Atmos. Environ. 41, 4734–4747. http://dx.doi.org/10.1016/j.atmosenv.2007.03.023.
Chiaradia, M., Gulson, B.L., James, M., Jameson, C.W., Johnson, D., 1997. Identification of secondary lead sources in the air of an urban environment. Atmos. Environ. 31, 3511–3521. http://dx.doi.org/10.1016/S1352-2310(97)00218-5.
Cong, Z., Kang, S., Luo, C., Li, Q., Huang, J., Gao, S., Li, X., 2011. Trace elements and lead isotopic composition of PM10 in Lhasa. Tibet. Atmos. Environ. 45, 6210–6215. http://dx.doi.org/10.1016/j.atmosenv.2011.07.060.
Dai, S., Li, D., Ren, D., Tang, Y., Shao, L., Song, H., 2004. Geochemistry of the late Permian No. 30 coal seam, Zhijin Coalfield of Southwest China: influence of a siliceous low-temperature hydrothermal fluid. Appl. Geochem 19, 1315–1330. http://dx.doi.org/10.1016/j.apgeochem.2003.12.008.
Díaz-Somoano, M., Kylander, M.E., López-Antón, M.A., Suárez-Ruiz, I., Martínez-Tarazona, M.R., Ferrat, M., Kober, B., Weiss, D.J., 2009. Stable lead isotope compositions in selected coals from around the world and implications for present day aerosol source tracing. Environ. Sci. Technol. 43, 1078–1085. http://dx.doi.org/10.1021/es801818r.
Doucet, F.J., Carignan, J., 2011. Atmospheric isotopic composition and trace metal concentration as revealed by epiphytic lichens. Atmos. Environ. 35, 3681–3690.
Duzgoren-Aydin, N.S., Li, X.D., Wong, S.C., 2004. Lead contamination and isotope signatures in the urban environment of Hong Kong. Environ. Int. 30, 209–217. http://dx.doi.org/10.1016/S0160-4120(03)00175-2.
Duzgoren-Aydin, N.S., 2007. Sources and characteristics of lead pollution in the urban environment of Guangzhou. Sci. Total. Environ. 385, 182–195. http://dx.doi.org/10.1016/j.scitotenv.2007.06.047.
Flament, P., Bertho, M.-L., Deboudt, K., Véron, A., Puskaric, E., 2002. European isotopic signatures for lead in atmospheric aerosols: a source apportionment based upon $^{206}Pb/^{207}Pb$ ratios. Sci. Total. Environ. 296, 35–57. http://dx.doi.org/10.1016/S0048-9697(02)00021-9.
Galer, S., Abouchami, W., 1998. Practical application of lead triple spiking for correction of instrumental mass discrimination. Mineral. Mag. 62A, 491–492. http://dx.doi.org/10.1180/minmag.1998.62A.1.260.
Gao, Z., Yin, G., Ni, S., Zhang, C., 2004. Geochemical features of the urban environmental lead isotope in chengdu city. Carsologica Sin. 23, 267–272 (in Chinese with English abstract).
Gioia, S.M.C.L., Pimentel, M.M., Tessler, M., Dantas, E.L., Campos, J.E.G., Guimarães, E.M., Maruoka, M.T.S., Nascimento, E.L.C., 2006. Sources of anthropogenic lead in sediments from an artificial lake in Brasília–central Brazil. Sci. Total. Environ. 356, 125–142. http://dx.doi.org/10.1016/j.scitotenv.2005.02.041.
Hinrichs, J., Dellwig, O., Brumsack, H.J., 2002. Lead in sediments and suspended particulate matter of the German Bight: natural versus anthropogenic origin. Appl. Geochem 17, 621–632. http://dx.doi.org/10.1016/S0883-2927(01)00124-X.
Komárek, M., Ettler, V., Chrastný, V., Mihaljevič, M., 2008. Lead isotopes in environmental sciences: a review. Environ. Int. 34, 562–577. http://dx.doi.org/10.1016/j.envint.2007.10.005.
Lee, C.S.L., Li, X., Zhang, G., Peng, X., Zhang, L., 2005. Biomonitoring of trace metals in the atmosphere using moss (*Hypnum plumaeforme*) in the Nanling

Mountains and the Pearl River Delta, Southern China. Atmos. Environ. 39, 397–407. http://dx.doi.org/10.1016/j.atmosenv.2004.09.067.
Lee, C.S., Li, X., Shi, W., Cheung, S.C., Thornton, I., 2006. Metal contamination in urban, suburban, and country park soils of Hong Kong: a study based on GIS and multivariate statistics. Sci. Total. Environ. 356, 45–61. http://dx.doi.org/10.1016/j.scitotenv.2005.03.024.
Li, F.L., 2008. Biogeochemical Behavior of Heavy Metals in Vegetable Soils in the Suburb of Guiyang (Karst Area) and the Relation with Green Vegetable Produce. Ph.D. dissertation. Graduate School of CAS, Guiyang (in Chinese with English abstract).
Li, F.L., Liu, C.-Q., Yang, Y.G., Bi, X.Y., Liu, T.Z., Zhao, Z.Q., 2012. Natural and anthropogenic lead in soils and vegetables around Guiyang city, southwest China: a Pb isotopic approach. Sci. Total. Environ. 431, 339–347. http://dx.doi.org/10.1016/j.scitotenv.2012.05.040.
Liu, G.S., Hong, Y.T., Piao, H.C., Zeng, Y.Q., 1996. Study on sources of sulfur in atmospheric particulate matter with stable isotope method. China Environ. Sci. 16, 426–429 (in Chinese with English abstract).
Li, X., Zhang, Y., Tan, M., Liu, J., Bao, L., Zhang, G., Li, Y., Iida, A., 2009. Atmospheric lead pollution in fine particulate matter in Shanghai, China. J. Environ. Sci. 21, 1118–1124. http://dx.doi.org/10.1016/S1001-0742(08)62390-6.
Mihaljevič, M., Ettler, V., Strnad, L., Šebek, O., Vonásek, F., Drahota, P., Rohovec, J., 2009. Isotopic composition of lead in Czech coals. Int. J. Coal. Geol. 78, 38–46. http://dx.doi.org/10.1016/j.coal.2008.09.018.
Mukai, H., Furuta, N., Fujii, T., Ambe, Y., Sakamoto, K., Hashimoto, Y., 1993. Characterization of sources of lead in the urban air of Asia using ratios of stable lead isotopes. Environ. Sci. Technol. 27, 1347–1356. http://dx.doi.org/10.1021/es00044a009.
Mukai, H., Tanaka, A., Fujii, T., Nakao, M., 1994. Lead isotope ratios of airborne particulate matter as tracers of long-range transport of air pollutants around Japan. J. Geophys. Res.-Atmos 99, 3717–3726. http://dx.doi.org/10.1029/93JD02917.
Mukai, H., Tanaka, A., Fujii, T., Zeng, Y., Hong, Y., Tang, J., Guo, S., Xue, H., Sun, Z., Zhou, J., Xue, D., Zhao, J., Zhai, G., Gu, J., Zhai, P., 2001. Regional characteristics of sulfur and lead isotope ratios in the atmosphere at several Chinese urban sites. Environ. Sci. Technol. 35, 1064–1071. http://dx.doi.org/10.1021/es001399u.
Outridge, P.M., Hermanson, M.H., Lockhart, W.L., 2002. Regional variations in atmospheric deposition and sources of anthropogenic lead in lake sediments across the Canadian Arctic. Geochim. Cosmochim. Acta 66, 3521–3531.
Sturges, W.T., Barrie, L.A., 1987. Lead 206/207 isotope ratios in the atmosphere of North-America as tracers of United-States and Canadian emissions. Nature 329, 144–146. http://dx.doi.org/10.1038/329144a0.
Sturges, W.T., Barrie, L.A., 1989. The use of stable lead 206/207 isotope ratios and elemental composition to discriminate the origins of lead in aerosols at a rural site in eastern Canada. Atmos. Environ. 23, 1645–1657. http://dx.doi.org/10.1016/0004-6981(89)90049-8.
Wang, H.Y., 1993. Geochemistry of Pb-Zn mineralization in Guizhou. Guizhou Geol. 10, 272–280 (in Chinese with English abstract).
Wang, W., Liu, X., Zhao, L., Guo, D., Tian, X., Adams, F., 2006. Effectiveness of leaded petrol phase-out in Tianjin, China based on the aerosol lead concentration and isotope abundance ratio. Sci. Total. Environ. 364, 175–187. http://dx.doi.org/10.1016/j.scitotenv.2005.07.002.
Weiss, D., Shotyk, W., Kempf, O., 1999. Archives of atmospheric lead pollution. Naturwissenschaften 86, 262–275. http://dx.doi.org/10.1007/s001140050612.
Widory, D., Roy, S., Le Moullec, Y., Goupil, G., Cocherie, A., Guerrot, C., 2004. The origin of atmospheric particles in Paris: a view through carbon and lead isotopes. Atmos. Environ 38, 953–961. http://dx.doi.org/10.1016/j.atmosenv.2003.11.001.
Wong, C.S.C., Li, X.D., Zhang, G., Qi, S.H., Peng, X.Z., 2003. Atmospheric deposition of heavy metals in the Pearl River Delta, China. Atmos. Environ. 37, 767–776. http://dx.doi.org/10.1016/S1352-2310(02)00929-9.
Xu, H.M., Cao, J.J., Ho, K.F., Ding, H., Han, Y.M., Wang, G.H., Chow, J.C., Watson, J.G., Khol, S.D., Qiang, J., Li, W.T., 2012. Lead concentrations in fine particulate matter after the phasing out of leaded gasoline in Xi'an, China. Atmos. Environ. 46, 217–224. http://dx.doi.org/10.1016/j.atmosenv.2011.09.078.
Zhao, Z.Q., Liu, C.Q., Zhang, W., Wang, Q.L., 2011. Historical lead pollution in the central region of Guizhou province, China: a record of lead stable isotopes of lake sediments. Appl. Geochem 26, S267–S270. http://dx.doi.org/10.1016/j.apgeochem.2011.03.121.
Zheng, J., Tan, M., Shibata, Y., Tanaka, A., Li, Y., Zhang, G., Zhang, Y., Shan, Z., 2004. Characteristics of lead isotope ratios and elemental concentrations in PM10 fraction of airborne particulate matter in Shanghai after the phase-out of leaded gasoline. Atmos. Environ. 38, 1191–1200. http://dx.doi.org/10.1016/j.atmosenv.2003.11.004.
Zhu, B.Q., 1995. The mapping of geochemical provinces in China based on Pb isotopes. J. Geochem. Explor 55, 171–181. http://dx.doi.org/10.1016/0375-6742(95)00011-9.
Zhu, B.Q., Chen, Y.W., Peng, J.H., 2001. Lead isotope geochemistry of the urban environment in the Pearl River Delta. Appl. Geochem 16, 409–417. http://dx.doi.org/10.1016/S0883-2927(00)00047-0.
Zhu, B.Q., Chen, Y.W., Chang, X.Y., 2003. Application of Pb isotopic mapping to environment evaluation in China. Chem. Spec. Bioavailab. 14, 49–56. http://dx.doi.org/10.3184/095422902782775335.
Zhu, L., Tang, J., Lee, B., Zhang, Y., Zhang, F., 2010. Lead concentrations and isotopes in aerosols from Xiamen, China. Mar. Pollut. Bull. 60, 1946–1955. http://dx.doi.org/10.1016/j.marpolbul.2010.07.035.
Zhu, Z., Sun, G., Bi, X., Li, Z., Yu, G., 2013. Identification of trace metal pollution in urban dust from kindergartens using magnetic, geochemical and lead isotopic analyses. Atmos. Environ. 77, 9–15.