



Historical lead pollution in the central region of Guizhou province, China: A record of lead stable isotopes of lake sediments

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ABSTRACT

Economic reform in China since 1978 has accelerated economic development nationwide hugely, but has also brought about some environmental pollution. In order to identify the primary Pb source to the atmosphere in the central Guizhou region, Pb isotopic ratios in the acid soluble fraction of sediment from Hongfeng Lake were investigated. Lead isotopes in the lake sediments record the history of regional atmospheric Pb pollution. Before the economic reform in 1978, the $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{206}\text{Pb}/^{207}\text{Pb}$ ratios in the leachates of lake sediments were constant, with a range of 2.0060 to 2.0117 and of 1.2314 to 1.2355, respectively. In the early period of economic reform (1978 to 1988), with the rapid industrial growth in Guizhou province, the acid soluble Pb isotope ratios in the lake sediments changed sharply: the $^{208}\text{Pb}/^{206}\text{Pb}$ ratios increased from 2.0212 to about 2.05, while the $^{206}\text{Pb}/^{207}\text{Pb}$ ratios decreased from 1.2251 to 1.2060. Emissions from Pb-ore-related industries are suggested to be the major pollution source of Pb in this period. Due to output from a local power plant since 1988, the isotope ratios of the acid soluble Pb in sediments in 1990s are characterized by a little higher radiogenic Pb ($^{208}\text{Pb}/^{206}\text{Pb} = 2.0340\text{--}2.0400$; $^{206}\text{Pb}/^{207}\text{Pb} = 1.2122\text{--}1.2158$) than for the 1980s.

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1. Introduction

Lead has a detrimental effect on human health. It is thus imperative to understand the atmospheric deposition of Pb on the surface environment. The Pb isotope technique has been widely used to decipher the primary sources and deposition patterns of atmospheric Pb in different archives (Weiss et al., 1999 and references therein). Among these archives, lake sediment can provide high-resolution information about atmospheric Pb pollution history. Therefore, lake sediments have been comprehensively investigated in North America and Europe. However, research on lake sediment in China is scarce. Based on cores from Liangzi lake in Hubei, China, Lee et al. (2008) found that the Pb isotopes in lake sediment reflected the mining history of China. Most environmental Pb isotope research in China has focused on the airborne particulate matter in urban environments (e.g. Chen et al., 2008; Duzgoren-Aydin, 2007; Li et al., 2009; Mukai et al., 1993, 2001). Though Guizhou is an economically undeveloped province of China, it is a major coal-producing province and one of the most important industrial bases of China. Coal combustion has caused atmospheric problems such as acid precipitation in Guizhou (Han and Liu, 2006; Xiao and Liu, 2002). Hongfeng Lake (Fig. 1), an artificial reservoir located 25 km from Guiyang, the capital of Guizhou province, was built in 1960; hence the operation history

of this reservoir spans the period of fast development in Guizhou. The objective of this paper is to identify the temporal change in anthropogenic Pb pollution in central Guizhou region using the Pb isotopic composition of sediments from Hongfeng Lake.

2. Materials and methods

The sediment core was collected in 2002 from the central area of Hongfeng Lake (Fig. 1) using a gravity corer. Total depth of the sampled profile is 37 cm. The core was sliced in 2 cm thick intervals for the first 4 cm and at 1 cm intervals for the remaining length.

As the main purpose of this study was to identify the pollution source of Pb in air, only the acid soluble fraction of Pb in the sediments was extracted for analysis. Sediment was ultrasonically leached by 4% HNO_3 . Previous researches (Gioia et al., 2006; Zhu et al., 2001) have shown that this acid soluble fraction provided separation of pollution Pb from geogenic Pb without losing isotopic information.

The Pb concentrations were measured by an inductively coupled plasma mass spectrometer, with a precision of better than 10%. Lead was separated using the method of Zhu et al. (2001), and then its isotopic ratios were measured by a multi-collector inductively coupled plasma mass spectrometer (Nu Plasma), using the method of Belshaw et al. (1998). Over the period of the experiment, the values measured for the standard SRM-981 ($^{206}\text{Pb}/^{204}\text{Pb}$, 16.937 ± 0.005 ; $^{207}\text{Pb}/^{204}\text{Pb}$, 15.492 ± 0.006 ;

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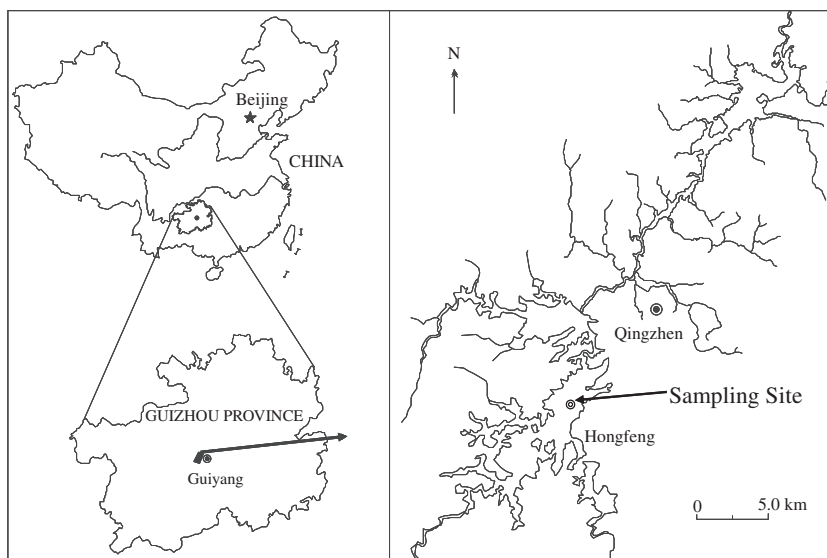


Fig. 1. Sketch map showing the locations of Hongfeng Lake and the sampling sites.

$^{208}\text{Pb}/^{204}\text{Pb}$, 36.702 ± 0.020 ; $^{208}\text{Pb}/^{206}\text{Pb}$, 2.16689 ± 0.00063 ; $^{207}\text{Pb}/^{206}\text{Pb}$, 0.91465 ± 0.00012) were consistent with the recalibrated values.

3. Results and discussion

The Pb concentrations and Pb isotope ratios ($^{280}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, $^{206}\text{Pb}/^{204}\text{Pb}$, $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{206}\text{Pb}/^{207}\text{Pb}$) of the leachates for all samples are listed in Table 1. Most of the Pb concentrations are in the range of 28 mg/kg to 40 mg/kg, and there is no apparent correlation between the Pb concentration and the sample depth. The Pb isotope ratios are variable: $^{206}\text{Pb}/^{207}\text{Pb}$ ratio decreases upward from about 1.23 to about 1.21 while $^{208}\text{Pb}/^{206}\text{Pb}$ ratio increases from about 2.00 to about 2.03.

3.1. Dating of the samples

The lake sediments can be clearly distinguished from the bed soil by sample color. Thus it is possible to be sure that the core went to the bottom of the profile. The average sedimentation rate was calculated using the accumulation time (1960–2000). The calculated accumulation rate was 11.4 mm/a, which was a little higher than the previously reported value using the ^{137}Cs method (9.3 ± 0.7 mm/year, Wan et al., 1991). This discrepancy may come from the difference of sampling sites. The average rate is temporarily used to calculate the age of each sample, although it is known that the accumulation rate might have changed during the sediment deposition period.

3.2. The temporal variation of Pb isotopic ratios and its implication

Fig. 2 shows the temporal evolution of $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios using the calculated ages. The record can be divided into three periods: (a) 1960–1977, in the depth range of 22 cm to 37 cm; (b) 1978–1988, with a depth of 12 cm to 21 cm; (c) 1990–2000, in the depth range of 0 cm to 11 cm. In the period from 1960 to 1977, the Pb isotopic ratios did not change, with the $^{208}\text{Pb}/^{206}\text{Pb}$ ratio in the range of 2.0060 to 2.0117 and $^{206}\text{Pb}/^{207}\text{Pb}$ of 1.2314 to 1.2355. In the period from 1978 to 1988, the Pb isotopic ratios changed sharply: $^{208}\text{Pb}/^{206}\text{Pb}$ ratio increased from 2.0212 to about 2.05 with a peak value of 2.0505, while the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio decreased from 1.2251 to 1.2060. In the period from 1990 to

2000, the Pb isotopic ratios stabilized again, with $^{208}\text{Pb}/^{206}\text{Pb}$ in the range of 2.0340–2.0400 and $^{206}\text{Pb}/^{207}\text{Pb}$ of 1.2122–1.2158. The temporal variation of Pb isotopic ratios in the leachates was coincident with the development history of the Guizhou economy. In 1978, Guizhou underwent fast development. Simultaneously, the Pb isotopic compositions of the lake sediments changed, indicating input of Pb from new sources into the lake.

3.3. Identification of the major pollution sources

The $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios of the samples are plotted in Fig. 3. Data from Pb–Zn ore samples from Guizhou province (Wang, 1993), vehicle exhaust and cinder from Guiyang city are plotted in the figure to decipher the major sources of Pb. Rainwater and dust samples from Guiyang city are also included. The Pb isotopic compositions in the leachate were all characterized by binary mixing, one end member likely to be vehicle exhaust or Pb-bearing ores, and the other to be coal combustion. As indicated by the gray arrow in Fig. 3, from the 1960s to 1980s Pb isotopic ratios of the leachates changed continually, deviating from the end member of coal combustion, towards the end member of vehicle exhaust or Pb-bearing ores. This implies that the Pb–Zn ore-related emission or vehicle exhaust is probably the major atmospheric Pb source in 1980s. In another project (Zhao et al., in preparation) it was found that most of the atmospheric Pb in the Guiyang area originated from industrial emissions, in contrast to the findings of Mukai et al. (1993, 2001). The small increase in $^{206}\text{Pb}/^{207}\text{Pb}$ and the small decrease in $^{208}\text{Pb}/^{206}\text{Pb}$ from 1988 to 1990 is probably the result of increasing input of local coal combustion since 1988 from the Qingzhen power plant, the second largest power plant of Guizhou, located 6 km away from Hongfeng Lake. It is concluded that the Pb-bearing ore-related industrial emission is likely the major pollution source of regional atmospheric Pb in the period 1978–1988. In the 1990s, the contribution of coal combustion has increased, indicating the influence of the Qingzhen power plant.

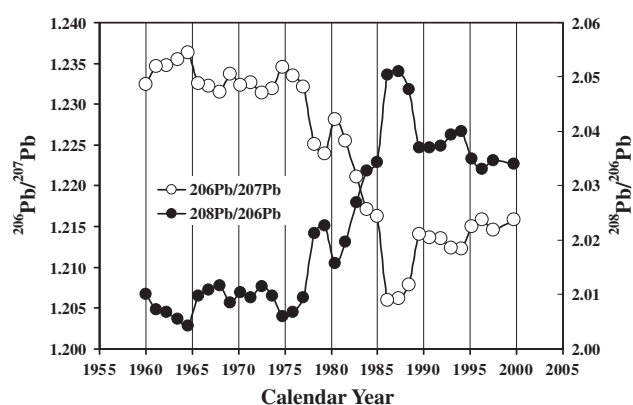
4. Conclusions

Using the calculated ages of the sliced sediment samples from Hongfeng Lake, based on the assumption that the sediments were accumulated on a stable rate, temporal evolution of Pb isotope

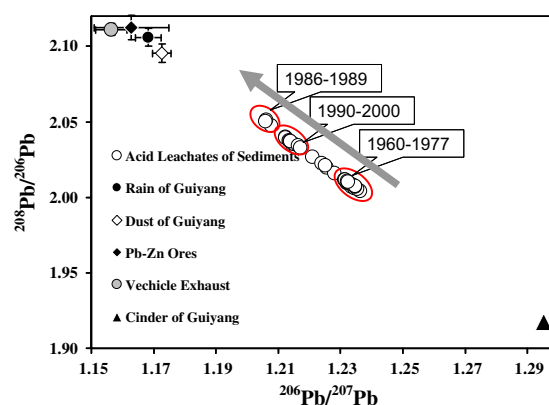
Table 1

The Pb concentrations and Pb isotopic compositions of the acid soluble fraction of the sediments from Hongfeng Lake and that from other materials.

ID	Depth (cm)	Pb (mg/kg)	$^{208}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{206}\text{Pb}$	$^{206}\text{Pb}/^{207}\text{Pb}$
<i>Lake sediments</i>							
SHF-1-1	2	27.6	38.889	15.726	19.121	2.0340	1.2158
SHF-1-2	4	44.3	38.848	15.720	19.094	2.0346	1.2146
SHF-1-3	5	30.0	38.857	15.720	19.113	2.0330	1.2158
SHF-1-4	6	25.6	38.867	15.720	19.099	2.0350	1.2150
SHF-1-5	7	28.4	38.869	15.718	19.053	2.0400	1.2122
SHF-1-6	8	43.0	38.866	15.719	19.058	2.0394	1.2124
SHF-1-7	9	32.0	38.864	15.719	19.075	2.0373	1.2135
SHF-1-8	10	34.6	38.861	15.719	19.078	2.0369	1.2137
SHF-1-9	11	35.1	38.876	15.720	19.084	2.0371	1.2140
SHF-1-10	12	34.3	38.876	15.719	18.986	2.0476	1.2079
SHF-1-11	13	61.0	38.896	15.723	18.964	2.0510	1.2062
SHF-1-12	14	42.7	38.871	15.719	18.957	2.0505	1.2060
SHF-1-13	15	32.9	38.899	15.721	19.122	2.0343	1.2163
SHF-1-14	16	34.4	38.890	15.719	19.132	2.0327	1.2171
SHF-1-15	17	31.2	38.907	15.720	19.195	2.0269	1.2211
SHF-1-16	18	33.5	38.935	15.732	19.280	2.0196	1.2256
SHF-1-17	19	34.4	38.935	15.727	19.315	2.0158	1.2282
SHF-1-18	20	31.9	38.931	15.726	19.248	2.0226	1.2240
SHF-1-19	21	38.2	38.946	15.728	19.268	2.0212	1.2251
SHF-1-20	22	30.1	38.942	15.729	19.379	2.0095	1.2321
SHF-1-21	23	38.5	38.934	15.728	19.401	2.0068	1.2335
SHF-1-22	24	31.1	38.984	15.742	19.434	2.0060	1.2346
SHF-1-23	25	30.2	38.959	15.736	19.384	2.0098	1.2319
SHF-1-24	26	36.3	38.982	15.738	19.379	2.0116	1.2314
SHF-1-25	27	36.9	38.970	15.733	19.394	2.0095	1.2326
SHF-1-26	28	41.8	38.975	15.731	19.386	2.0104	1.2323
SHF-1-27	29	52.1	38.986	15.734	19.410	2.0085	1.2337
SHF-1-28	30	29.2	38.974	15.732	19.373	2.0117	1.2315
SHF-1-29	31	30.9	38.985	15.734	19.387	2.0108	1.2322
SHF-1-30	32	32.5	38.970	15.731	19.390	2.0098	1.2326
SHF-1-31	33	32.8	38.987	15.733	19.451	2.0043	1.2363
SHF-1-32	34	23.7	38.988	15.735	19.440	2.0055	1.2355
SHF-1-33	35	27.8	38.979	15.731	19.424	2.0068	1.2348
SHF-1-34	36	27.4	38.986	15.731	19.423	2.0073	1.2346
SHF-1-35	37	28.2	38.968	15.729	19.386	2.0101	1.2325
Rainwater ^a (n = 10)	38.550	15.669	18.305	2.1060	1.1683		
Dust ^a (n = 16)	38.485	15.663	18.366	2.0955	1.1725		
Vehicle Exhaust ^a (n = 4)	38.142	15.621	18.068	2.1111	1.1564		
Cinder ^b (n = 1)	39.466	15.893	20.583	1.9174	1.2951		

^a Average values of samples from Guiyang, the STD values are plotted in Fig. 3.^b A cinder sampled from Guiyang power plant, to which the average values of 10 coals from Guizhou are similar.**Fig. 2.** The temporal evolution of Pb isotopic compositions in the acid soluble fraction of the sediments from Hongfeng Lake.

ratios of the acid soluble fraction in the lake sediment during the period of 1960–2000 was investigated. The results show that the Pb isotopes of lake sediments can record the history of atmospheric Pb pollution triggered by regional industrial development. Consistent with the slow development of Guizhou industries before the economic reform in 1978, the Pb isotope ratios of the leachates from lake sediments were stable in the period of 1960–1977. Since

**Fig. 3.** A plot of Pb isotopic ratios in the acid soluble fraction of the sediments from Hongfeng Lake, and for samples of dust, rain, vehicle exhaust, and cinder of Guiyang. The Pb-Zn ore samples of Guizhou province were calculated from Wang (1993).

the economic reform in 1978, with rapid industrial growth in Guizhou province, the leachate Pb isotope ratios of lake sediments changed sharply. Lead-bearing ore-related industrial emissions are suggested to be the major source of regional atmospheric Pb pollution in the early period of economic reforms. Due to the

influence of a local power plant since 1988, Pb isotope ratios in the acid soluble fraction of lake sediments in the 1990s were characterized by slightly higher radiogenic Pb than the 1980s.

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