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Lead Content and Isotope Composition in Surface Sediments in Western Xiamen Bay and Its Vicinity: Implication for Possible Source

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Lead contents and isotope compositions ($^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$) in surface sediments in western Xiamen Bay and its vicinity in South Fujian, China, were measured to assess the spatial variations and to identify Pb sources. The spatial variations of Pb contents in sediments were confirmed and enrichment factors suggested deficiency to minimal enrichment of anthropogenic lead in sediments. Lead isotopic ratios ranged from 1.173-1.186 with the mean value of 1.181 for $^{206}Pb/^{207}Pb$ and from 2.078-2.101 with the mean value of 2.094 for $^{208}Pb/^{206}Pb$, respectively. The Pb isotope ratios indicated the homogenization of isotope compositions and confirmed that vehicular Pb was not the primary Pb contamination sources in the sediments in the studied region. Chinese coal and Fujian Pb-Zn deposits might be the potential anthropogenic Pb sources and Fujian basalts and granite are the important natural Pb source.

Key Words: Sediment, Pb content, Pb isotope composition, Source identification.

INTRODUCTION

Lead is used widely in many industrial processes and occurs as an important contaminant in all environmental compartments (soils, water, the atmosphere, sediments and living organisms). Lead contamination may result both from its persistence and from its present and past numerous sources such as smelting, combustion of leaded gasoline, or applications of lead-contaminated media. In 2009, production of recoverable lead from mining operations was 1690, 516 and 400 thousand metric tons by China, Australia and the USA, respectively[1]. Lead has four stable isotopes: ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb, the last three with radiogenic origins from ^{238}U, ^{235}U and ^{232}Th, respectively[2-4]. Since each source of Pb can have a distinct or sometimes overlapping isotopic ratio range and physico-chemical fractionation processes do not alter the Pb isotopic composition of Pb sources, therefore the use of the lead isotope ratio is referred to as "lead fingerprinting"[2-4]. Lead concentration and isotopes have been widely used to trace environmental Pb pollution and to identify the Pb sources[2-4]. Lead isotope signatures have been successfully used on the sediment investigations to trace or identify the lead sources[4-7].

Western Xiamen Bay located in South Fujian, China, is a semi-enclosed bay and is adjacent to Jiulong River Estuary. The rapid development of the Xiamen Special Economic Zone set up in 1980s has resulted in great environmental stresses around western Xiamen Bay and its adjacent areas. Some researches on sediment investigations show a serious situation with As, Pb and Zn and those may have ecological risks[8-10]. In the present study, surface sediments and suspended particle matters were collected from western Xiamen Bay and the Jiulong River Estuary. Lead contents and isotopic ratios were analyzed. The purpose of this study is to assess the spatial variations and to identify the metal sources for the surface sediment from western Xiamen Bay and its vicinity using Pb contents and Pb isotope tracing technique.

EXPERIMENTAL

Field sampling for surface sediments (< 5 cm) was conducted in August 2008. The sampling stations in western Xiamen Bay and the Jiulong River Estuary are shown in Fig. 1. Stns 1-14 and Stns 15-27 were located in the Jiulong River Estuary and western Xiamen Bay, respectively. Eight samples of suspended particle matters (SPM) were collected by 0.45-μm filtration film. Following the field work, small stones and conch debris in sediment samples were removed by hand and particle-size fractions of sediment samples were isolated using 63 μm nylon mesh, got the < 63 μm fraction of sediment samples. The dried samples were then ground to a powder

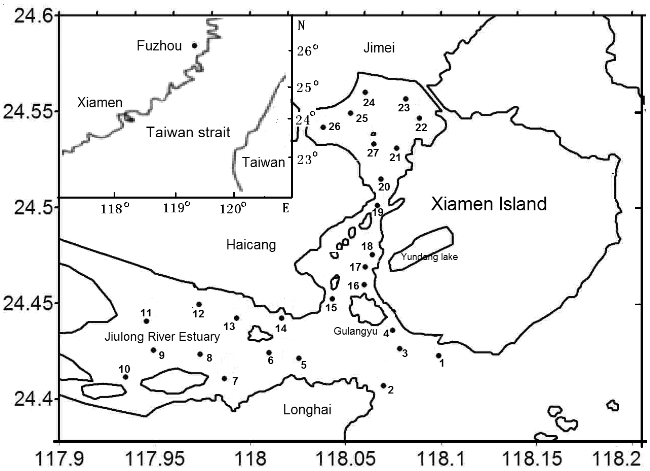

Fig. 1. Sampling stations in western Xiamen Bay and the Jiulong River Estuary

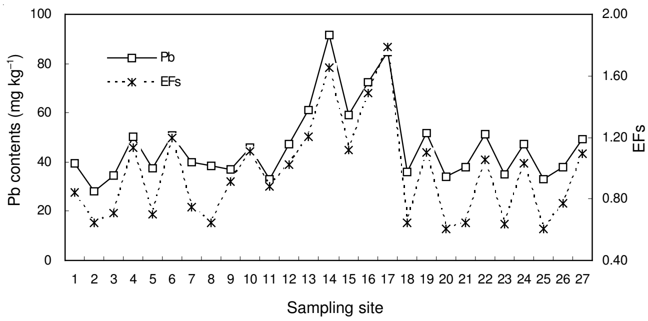

Fig. 2. Lead contents and enrichment factor values in the sediments from western Xiamen Bay and the Jiulong River Estuary

with a mortar and pestle, sieved through a 250 mesh sieve and kept in pre-cleaned containers for future use. The filtration film samples were dried at 40 ºC and also kept in pre-cleaned containers for future use.

Metal and lead isotopic analysis: Duplicate sediment samples were analyzed for metal content using HCl-HNO_3-HF-$HClO_4$ mixture digestion. Suspended particle matters were digested as sediment samples for lead isotopic analysis. Precision and accuracy were verified using standard reference materials from the National Research Center for Geoanalysis, China (GSD-1 and GSD-4 sediment). Differences in metal concentrations between this study and the certified values were generally < 10 %. The water used for dilution and dissolution was purified using a Millipore deionizing system at 18.2 MΩ. HCl, HF, $HClO_4$ and HNO_3 were bought directly as ultra-pure reagents. Solutions from digested sediments were stored in 25 mL high density polyethylene sample bottles at 4 ºC until analysis. Lead and Al were measured using a Perkin-Elmer ICP-OES SCIEX Optima5300DV.

Lead isotopic analyses were carried out using a Perkin-Elmer ICP-QMS SCIEX Elan 9000 as described in the literatures[11-13]. Precision and accuracy were verified using a standard reference material from the National Institute of Standards and Technology (SRM 981 common lead isotopic material). Repeated measurements of the SRM 981 Pb reference material over different analytical sessions yielded the following mass ratios: $^{207}Pb/^{206}Pb$= 0.913 ± 0.004 and $^{208}Pb/^{206}Pb$ = 2.150 ± 0.008. The standard accepted values are: $^{207}Pb/^{206}Pb$ = 0.9146 and $^{208}Pb/^{206}Pb$ = 2.1681. Pb isotopic ratios reported in this work were calibrated using SRM 981 which was re-analyzed after every second sample.

RESULTS AND DISCUSSION

Lead contents in the surface sediments: Lead contents in the surface sediments from western Xiamen Bay and the Jiulong River Estuary are shown in Fig. 2. Lead contents ranged from 28.2-91.9 mg kg^{-1} with the mean 45.3 (± 15.9, std. deviation) mg kg^{-1} in the surface sediments from the Jiulong River Estuary and the highest Pb content (91.9 mg kg^{-1}) was found in the sampling site 14 (Fig. 2). Lead contents ranged from 33.1-84.6 mg kg^{-1} with the mean 48.4 (± 15.8, std. deviation) mg kg^{-1} in the surface sediments from the western Xiamen Bay and the highest Pb content (84.6 mg kg^{-1}) was found in the 16th sampling site (Fig. 2). Fig. 2 also showed the spatial variations of Pb contents in sediments from different sampling sites. Fig. 2 also showed that Pb content in the sampling site 13-17 was obviously higher than them in the other sites. The sampling site 13-17 is around the Songyu coal burning power plant, located in Haicang (Fig. 1), which may release Pb-bearing particulates into sediments through atmospheric deposition, wastewater and runoff.

Lead contents in the sediments from some literatures and the national standards for marine sediment quality, P.R. China were listed in Table-1. Table-1 shows that the lead contents in present study were consistent with them of the previous reports[8-10]. Lead contents in Quanzhu Bay, locates next to Xiamen Bay, were higher than them of our study (Table-1)[14]. Lead contents in our study were also consistent with them in sediments from Peral River Estuary report by Wang *et al.*[15] and higher than them in sediments from Yangtze river estuary report by An *et al.*[16], in River Estuary and Bay in China (Table-1). In generally, Pb contents in our study were higher than them in the reports[17-19] and less than them in sediments from other researches[20-23] in Table-1. Lead contents in our study were lower than the secondary standard of marine sediment quality, P.R. China[24], suggesting no serious lead contamination in the studied region.

TABLE-1
LEAD CONTENTS (mg kg^{-1}) IN THE SEDIMENTS IN THE STUDIED AREA WITH THOSE FROM SOME LITERATURES

Region	Pb	Ref.
Western Xiamen Bay (China)	46.8 ± 15.6	This study
Western Xiamen Bay (China)	50	8
Western Xiamen Bay (China)	52	9
Western Xiamen Bay (China)	21.4-114	10
Quanzhou Bay (China)	105-242	14
Peral River Estuary (China)	37.83	15
Yangtze river estuary (China)	21.9 ± 4.1	16
Mandovi estuary(India)	4.5-46.5	17
Mazatlán Harbor (Mexico)	49.6-54.0	18
Lake Victoria (Tanzania)	29.6 ± 1.6	19
Kaohsiung Harbor (Taiwan)	9.5-470	20
Keratsini Harbor (Greece)	521-1263	21
Taranto Gulf (Italy)	57.8	22
Montevideo harbor (Uruguay)	44-128	23
Primary standard	60	24
Secondary standard	130	24
Tertiary standard	250	24

In order to differentiate anthropogenic sources from natural origin of Pb in surface sediments, enrichment factor (EF) was used for data analysis in the present study. The enrichment factor or lead were calculated using the follow equation:

$$\text{Enrichment factor (EF)} = \frac{\left(\dfrac{C_{Pb}}{C_{Al}}\right)_{Sample}}{\left(\dfrac{C_{Pb}}{C_{Al}}\right)_{Background}}$$

where $(C_{Pb}/C_{Al})_{sample}$ is the ratio of Pb to Al in the samples and $(C_{Pb}/C_{Al})_{background}$ is the natural background value of the ratio of Pb to Al[25]. The elemental contents in the local soil were used in this study as the background (46.8 mg kg^{-1} for Pb and 8.98 % for Al)[26]. The enrichment factors ranged from 0.60 to 1.79 with the mean value of 0.96. According to the enrichment factor categories based on the previous research[25]: enrichment factor < 2 means deficiency to minimal enrichment. Therefore, the enrichment of anthropogenic lead was not serious in the studied region.

Lead isotopic compositions in the surface sediments and the suspended particle matters: Lead isotopic compositions in the studied sediments and suspended particle matters were shown in Table-2 and Fig. 3. Table-2 shows that the range and mean (± SD) values were 1.173-1.186 (1.178 ± 0.004) for $^{206}Pb/^{207}Pb$ and 2.078-2.101 (2.090 ± 0.007) for $^{208}Pb/^{206}Pb$, respectively. The relative deviations of the maximum and minimum value were less than 2 % (Table-2), suggesting homogenization effect on Pb isotopic ratios from different sampling sites. It is consistent with the reported by Choi *et al.*[6]. The Pb isotope ratios in the suspended particle matters ranged from 1.171-1.176 for $^{206}Pb/^{207}Pb$ and from 2.099-2.107 for $^{208}Pb/^{206}Pb$, indicating the difference of Pb sources between sediments and suspended particle matters.

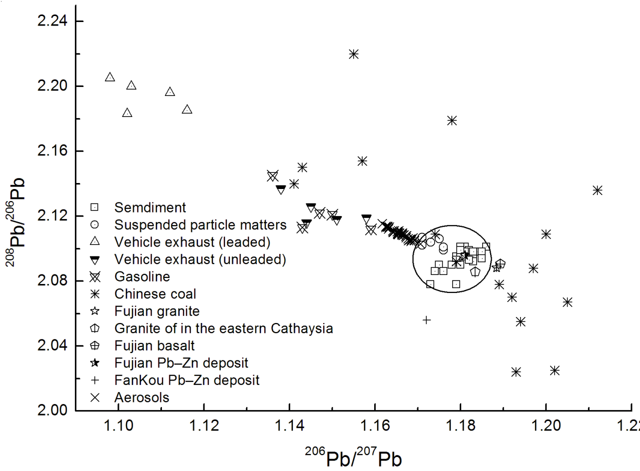

Fig. 3. Plot of $^{206}Pb/^{207}Pb$ *vs.* $^{208}Pb/^{206}Pb$. Sources data for vehicle exhaust (leaded/ unleaded) were from[33,34]; data for Chinese coal from[34] and (1993)[36]; data for Fujian granite and Fujian basalt from[31]; data for Granite of in the eastern Cathaysia and FanKou Pb-Zn deposit from[32]; data for Fujian Pb-Zn deposit from[28] and data for aerosols from[27]

Source identification using lead isotopic compositions: The Pb isotopic ratios ($^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$) in the potential natural sources in the literatures are also shown in Table-2 and Fig. 3. The Pb isotopic ratios ($^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$) in the studied sediments were different from them in aerosols in Xiamen, which had a slight low ratios of $^{206}Pb/$

TABLE-2
Pb ISOTOPIC COMPOSITIONS OF NATURAL BACKGROUND AND POLLUTION SOURCES

	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{206}Pb$	Ref.
Sediment	1.173-1.186 (1.181 ± 0.003)	2.078-2.101 (2.094 ± 0.006)	This study
SPM	1.171-1.176 (1.173 ± 0.002)	2.099-2.107 (2.104 ± 0.003)	This study
Aerosols	1.17058-1.16166 (1.16595)	2.10285-2.11544 (2.10897)	27
Natural sources			
Fujian granite	1.1884	2.0882	31
Fujian basalt	1.1893	2.0905	31
Granite of in the eastern Cathaysia	1.1834	2.0856	32
Uncontaminated soil	1.1952	2.0763	32
Granite in the Pearl River Delta	1.1842	2.0963	32
Volcanic rocks in Foshan	1.1993	2.0816	32
Anthropogenic sources			
Fujian Pb–Zn deposit	1.182-1.180 (1.181)	2.0921-2.0996 (2.0958)	28
Fankou Pb–Zn deposits	1.172	2.110	32
Vehicle exhaust(leaded gasoline)	1.098-1.112 (1.106)	2.183-2.205 (2.194)	33
Vehicle exhaust(unleaded gasoline)	1.138-1.158 (1.147)	2.116-2.137 (2.123)	33
Gasoline	1.143-1.159 (1.150)	2.112-2.121 (2.115)	33
vehicle exhaust	1.118-1.143(1.130)	2.141-2.151 (2.146)	34
vehicle exhaust(leaded) in Shanghai	1.110	2.194	35
vehicle exhaust(unleaded) in Shanghai	1.147	2.124	35
vehicle exhaust in the pearl river delta	1.160	2.085	23
Chinese coal	2.024-2.154 (2.089)	1.141-1.205 (1.182)	36
Coal in Shanghai (n = 23)	1.208-1.140 (1.163)	2.1111	33
Coal combustion dust in Shanghai	1.172-1.163 (1.167)	–	33
Coal fly ash in Shanghai (n = 3)	1.170-1.161 (1.166)	–	33
Coal combustion in Shanghai	1.1633	2.1111	35
Unburned coal	1.15-1.212 (1.181)	2.092-2.220 (2.157)	34
Metallurgic dust in Shanghai	1.1725	2.0768	35

^{207}Pb and high ratios of $^{208}Pb/^{206}Pb$[27]. The Pb isotopic ratios of suspended particle matters overlapped with aerosols and sediments (Fig. 3). The Pb isotopic ratios in the studied sediments lapped over them in granite of in the eastern Cathaysia and were closer to them from Fujian granite and Fujian basalts (Fig. 3). Therefore, Fujian basalts and granite might be the important potential natural sources.

Generally, industrial emissions, vehicle exhausts and coal combustion are the three major lead pollution sources in Chinese cities[2]. Therefore, the isotope ratios of the potential sources of anthropogenic Pb in literatures are also presented in Fig. 3. Fig. 3 shows that the Pb isotope ratios in the present study were consistent with them from Fujian Pb-Zn deposit and different from those in FanKou Pb-Zn deposit (Fig. 3). Gasoline and vehicular Pb were the most important Pb contamination sources for atmospheric particles during the period of the use of leaded petrol. Fig. 3 shows that Pb isotope ratios in the present study were different from those in oil combustion and vehicle exhaust (unleaded/leaded gasoline), which had lower $^{206}Pb/^{207}Pb$ ratios. After the ban of leaded gasoline, vehicle exhaust is not a significant anthropogenic Pb source[28]. 3.45×10^6 ton coal and 3.44×10^6 ton coal were used as industrial raw material and fuel coal in thermal power industry in 2006 in Xiamen, respectively[29], so coal is still the most important onetime energy in Xiamen. The combustion of coal releases harmful particulates, including Pb-bearing particulates, into the environment. For example, Songyu coal burning power plant locates in western Xiamen Bay, which may release Pb-bearing particulates into western Xiamen Bay and Jiulong River Estuary through atmospheric deposition, wastewater and runoff. Mukai *et al*.[30] reported that Chinese coal has wide variations in lead isotopic ratios. Fig. 3 shows that the Pb isotopic ratios in the studied sediments were in range of the Pb isotopic ratios in the Chinese coal. It can be speculated that the consumption of coal might play an important role in Pb accumulation in the studied sediments. Based on the Pb isotopic ratios, the Pb that accumulates in the sediments is a mixture of Pb derived from natural sources and anthropogenic sources (coal combustion, industrial emissions and others) and gasoline and vehicular Pb were not the primary sources of Pb contamination for the sediments.

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