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# Contamination and isotopic composition of Pb and Sr in offshore surface sediments from Jiulong River, Southeast China☆

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## ABSTRACT

Concentrations and isotopic compositions of Pb and Sr in the surface sediment samples from Jiulong River, Southeast China, were determined to trace the sources of Pb and Sr. The average concentrations of Pb and Sr were 110.9 mg/kg and 69.2 mg/kg, approximately 3.2 and 2.0 times of the local soil background values, respectively. Average 62.9% of total Pb and 36.8% of total Sr in the investigated surface sediment samples were extracted by 0.5 mol/L $HNO_3$. Pb and Sr presented slight contamination, and Pb showed low ecological risk for most of surface sediment samples in Jiulong River according to geo-accumulation index ($I_{geo}$) and potential ecological risk index (RI). The results of Pb isotopic compositions in sediment samples and potential sources showed that the Pb accumulated in the surface sediments of Jiulong River was mainly from parent material, coal combustion and Fujian Pb-Zn deposit, with the contribution rates of 34.4%, 34.0%, and 31.6%, respectively. The results of Pb isotopic compositions in 0.5 mol/L $HNO_3$-extraction suggested that dilute $HNO_3$-extraction was more sensitive in identifying anthropogenic Pb sources than total digestion. The results of Sr isotopic compositions showed that Sr accumulated in the surface sediments of Jiulong River estuary mainly derived from external source and natural source (parent material) with the contribution rates of 48.1% and 51.9%, respectively.

## 1. Introduction

Heavy metal pollution in sediments has attracted increasing public attention because of its harmful effects on human health (Li et al., 2012). Lead (Pb) was used widely in many aspects such as building with the development urbanization and industrialization (Cheng and Hu, 2010). Today, Pb has become one of the most widely dispersed poisonous metals in the world as a consequence of human's activities. Recently, strontium (Sr) has attracted considerable interest because it may bring a harmful effect to human health if the diet is low in calcium and protein (Khandare et al., 2015). It has been reported that coastal sediment can act as a sink as well as source for toxic metals (Chakraborty et al., 2012). It was widely recognized that sediment could be used to be an environmental indicator for heavy metal pollution so as to trace pollution sources of heavy metals in the overlying water (Soares et al., 1999).

Radiogenic isotopes are well known as powerful tracers. Variations of Pb and Sr isotopic ratios could suggest the sources of Pb and Sr with different isotopic compositions, respectively (Sun et al., 2011). Sr isotope is applied relatively later than Pb isotope as another environmental pollutant tracer. Pb and Sr concentrations and isotopic compositions have been widely used to evaluate the environmental pollution and trace the sources of Pb and Sr (Gulson et al., 2012; Xu et al., 2014; Dang et al., 2015; Bentahila et al., 2008). It has been reported that anthropogenic Pb was mainly related to the acid-extractable phases and natural Pb was mainly related to residual phase (Teutsch et al., 2001). The $^{87}Sr/^{86}Sr$ ratio is often employed in combining with Pb or other elemental isotopes to trace the sources of heavy metals (Bentahila et al., 2008).

Jiulong River is the second largest river of Fujian Province(SE China), with a total drainage basin area of 1.47 × $10^4$ $km^2$ and a total flow of 12.4 × $10^9$ $m^3/y$. It flows through Longyan, Zhangzhou and Xiamen regions, and acts as the important source

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of drinking, industrial and agricultural water for the above mentioned regions (Lin et al., 2011). North River and West River are the two major tributaries of Jiulong River, and the North River accounts for approximately two-thirds of the total flow (Chen et al., 2015). Besides millions of people living in the catchment basin, there are thousands of industrial enterprises, including lead-zinc mining, metal smelting and processing, coal-fired power plants, sewage treatment plants and pig farms, which inevitably result in a lot of discharged pollutants including heavy metals. It has been reported that Jiulong River has been polluted by heavy metals as a consequence of human activities (Wang et al., 2014; Zhang et al., 2014). However, it is still not clear about the sources of heavy metals in Jiulong River and the contribution rates of each source.

In this study, Pb and Sr concentrations and isotopic compositions in surface sediments of Jiulong River were determined to aim the objectives as follows: (i) to investigate Pb and Sr contamination in the sediments of Jiulong River; (ii) to identify the major sources of Pb and Sr in the sediments of Jiulong River and calculate the contribution rates of each source.

## 2. Materials and methods

### 2.1. Sampling and preparation

Fifty-three surface sediment samples (0–5 cm) in Jiiulong River were collected using a Van Veen grab sampler in October 2012 (Fig. 1: sites 1–17 from offshore of Jiulong River upstream, sites 18–32 from coastal wetland, and sites 33–53 from intertidal zone of Jiulong River estuary). The sampled sediments were sealed in clean plastic bags and stored at −20 °C for 24 h. Then the sediment samples were defrosted and air-dried at room temperature. The sediment samples were then ground using an agate pestle and mortar and filtered through a 63 μm nylon sieve. These sections (<63 μm) were sealed in clean plastic bags at 4 °C for future analysis because of the reason that heavy metals were strong associated with fine-grained sediments (Horowitz and Elrick, 1987).

### 2.2. Determination of Pb and Sr concentrations

All sediment samples were analyzed using both total digestion with $HCl-HNO_3-HF-HClO_4$ and partial extraction with 0.5 mol/L $HNO_3$. Concentrations of Pb and Sr in both total and $HNO_3$-extractable phases were determined by an inductively coupled plasma-mass spectrometry (ICP-MS) (ELAN9000, Perkin-Elmer, USA). Reagent blanks and sample replicates were included throughout the analysis, and the analytical precisions were better than 10%. Sediment reference materials (GBW07314, the State Oceanographic Administration of China) were analyzed with the same procedure as sediment samples. The recovery rates for Pb and Sr in the reference materials were around 95%–104%.

### 2.3. Determination of Pb and Sr isotopes

Sample preparation of Pb and Sr isotopic compositions was conducted in a clean laboratory of the Analytical Laboratory Beijing Research Institute of Uranium Geology. The separation and purification was processed according to analytical procedures of DZ/T0184.12–1997. Pb and Sr isotopic compositions in digests and Pb isotopic compositions in extracts were determined using VG354 thermal ionization mass spectrometry. Solutions of reference materials (NBS981 for Pb isotope and NBS987 for Sr isotope, National Bureau of Standards, USA) were determined before every five samples as standards for calibration and quality control. The measured $^{208}Pb/^{206}Pb$, $^{207}Pb/^{206}Pb$ and $^{207}Pb/^{204}Pb$ ratios of NBS981 were 2.1681 ± 0.0008, 0.91462 ± 0.00033 and 15.4910 ± 0.0097, respectively. The measured $^{87}Sr/^{86}Sr$ of NBS987 was 0.710220 ± 0.000015. In this study, 53 sediment samples were analyzed for Pb isotopic compositions and 14 sediment samples (from Jiulong River estuary) were analyzed for Sr isotopic compositions.

In order to trace the Pb and Sr accumulated in the sediments of Jiulong River, an environmental investigation within the catchment basin was performed. The soils within the basin developed mainly from granite and partly from rhyolite, tuff and purple rock. The

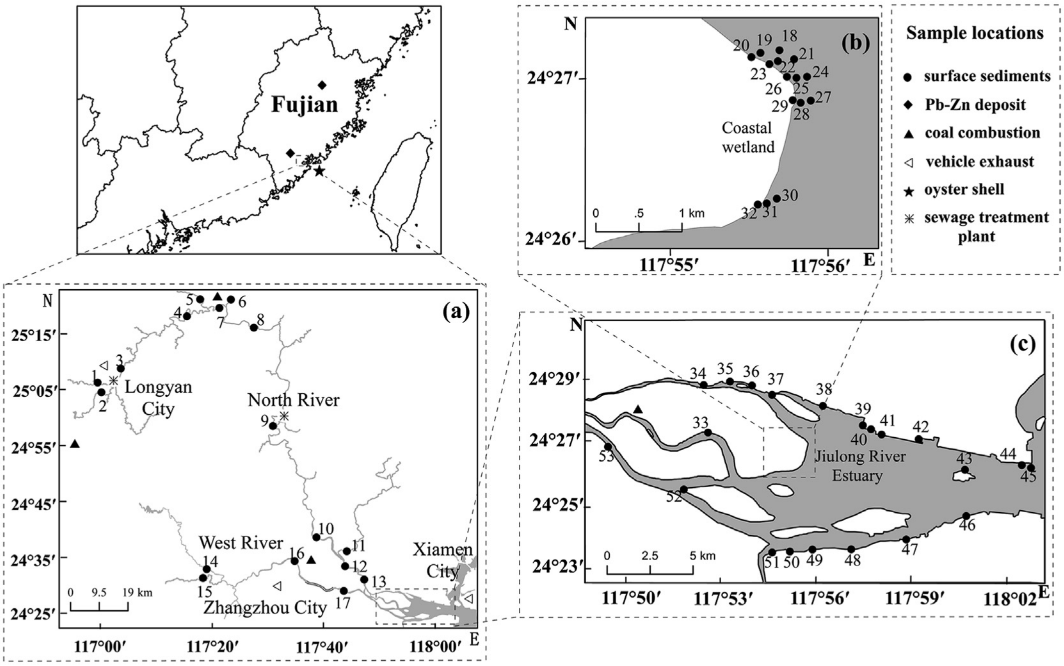

**Fig. 1.** Sample locations of surface sediments in Jiulong River (a) Upstream; (b)Coastal wetland; (c) Estuary.

parent material was chosen as the nature source. Fujian Pb-Zn deposit, coal combustion and vehicle exhaust were chosen as anthropogenic sources of Pb and Sr accumulated in the sediments according to the characteristic of Pb and Sr and the social environment of Jiulong River basin. Oyster shell was chosen as another source of Sr which represents the marine source due to the high concentrations of Sr in seawater.

Vehicle exhaust samples were collected from exhaust pipes of cars in some large parking lots in the basin (Hu et al., 2013). Coal combustion samples were collected from coal-fired power plants and some other coal-fired enterprises in the basin. Fujian Pb-Zn deposit samples were collected from Pb-Zn deposits in Longyan and Nanping. All of these samples were systematically analyzed for Pb and Sr isotopic compositions. Oyster shell samples were collected from Xiamen Sea which connected with Jiulong River estuary and they were systematically analyzed for Sr isotopic compositions.

## 3. Results and discussion

### 3.1. Pb and Sr concentrations in the surface sediments

Concentrations of total Pb and Sr in the offshore surface sediments from Jiulong River showed considerable variation (38.5–839.6 mg/kg for Pb and 39.5–130.0 mg/kg for Sr) with the mean of 110.9 mg/kg and 69.2 mg/kg, respectively (Fig. 2), which were nearly 3.2 and 2.0 times as high as the local background values of Pb (34.9 mg/kg) and Sr (34.0 mg/kg), respectively (Chen et al., 1992). The sediments from Jiulong upstream had significantly higher Pb (184.3 mg/kg) than those from coastal wetland (74.0 mg/kg) and Jiulong River estuary (77.8 mg/kg). The sediments from Jiulong River estuary had significantly higher Sr (92.8 mg/kg) than those from Jiulong upstream (59.7 mg/kg) and coastal wetland (46.8 mg/kg).

In fact, heavy metals presented differently in many forms such as acid-extractable and residual phase, and they have different mobility and toxicity (Gao et al., 2014). In this study, all sediment samples were extracted using 0.5 mol/L $HNO_3$ (Zhang et al., 2015) and the results were shown in Fig. 2. Average 62.9% (with the range of 27.2%–85.2%) of total Pb and 36.8% (with the range of 18.7%–72.8%) of total Sr in all investigated surface sediments from Jiulong River were extracted by 0.5 mol/L $HNO_3$. The dilute $HNO_3$-extractable Pb and Sr are weakly bonded with sediments, thus they are more mobile and easily bioavailable and may dissolve in the aqueous phase. The higher the proportion of Pb and Sr in the dilute $HNO_3$-extractable phase, the more mobile and bioavailable they are, and they have greater risk to the ecological environment. In summary, Pb was more mobile and had higher risk to the ecological environment than Sr in surface sediments of Jiulong River.

### 3.2. Assessment of Pb and Sr contamination

Geo-accumulation index ($I_{geo}$) is a quantitative indicator to reflect the pollution levels of heavy metals in sediments (Müller, 1969). The $I_{geo}$ values of Pb and Sr in the surface sediments of Jiulong River were calculated using Formula (1).

$$I_{geo} = \log_2[C_i/(k \times C_n)] \tag{1}$$

Where, $C_i$ is the measured concentration of Pb or Sr in surface sediments; $C_n$ is the geochemical background value of Pb or Sr in Fujian Province (34.9 mg/kg for Pb and 34.0 mg/kg for Sr) (Chen et al., 1992); and k is the correction factor for the value of background which may influenced by lithogenic effects, generally taken as 1.5. Seven classes of contamination were adopted according to the $I_{geo}$ values: non-contamination ($I_{geo}<0$), slight contamination ($0\le I_{geo}<1$), moderate contamination ($1\le I_{geo}<2$), moderate to strong contamination ($2\le I_{geo}<3$), strong contamination ($3\le I_{geo}<4$), strong to extreme contamination ($4\le I_{geo}<5$), and extreme contamination ($5\le I_{geo}$).

Potential ecological risk index (*RI*), first proposed by Hakanson, is an effective method to assess pollution level and potential ecological risk of contaminants including heavy metals in sediments (Hakanson, 1980). The potential ecological risk index of Pb in the surface sediments of Jiulong River was calculated using Formula (2).

$$E_r = T_r \times \frac{C_i}{C_n} \tag{2}$$

where, $E_r$ is the potential ecological risk index of Pb; $C_i$ is the

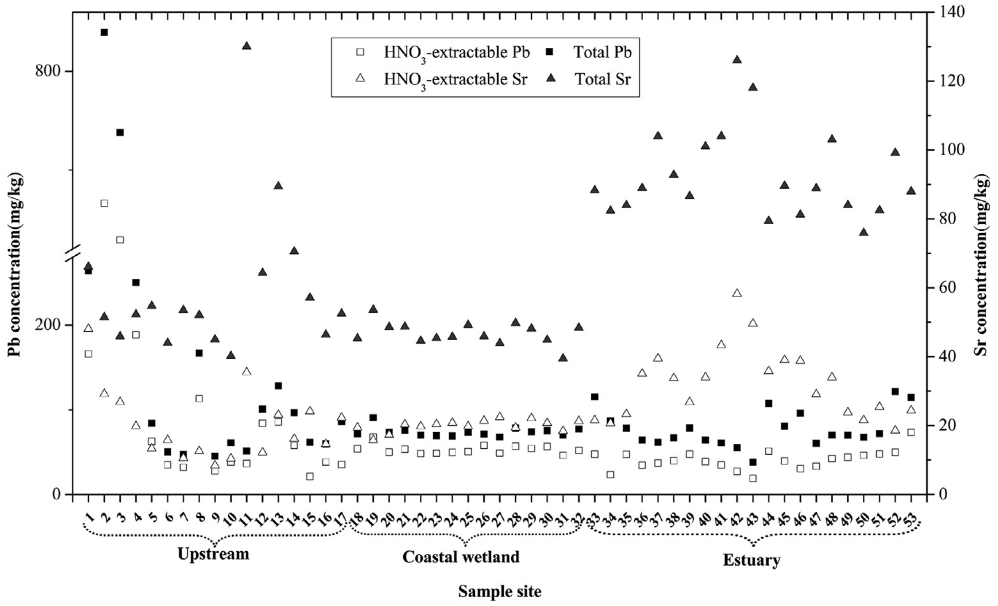

**Fig. 2.** Total and 0.5 mol/L $HNO_3$-extractable Pb and Sr concentrations in surface sediments of Jiulong River.

concentration of Pb in surface sediments; $C_n$ is the geochemical background value of Pb (34.9 mg/kg) (Chen et al., 1992); $T_r$ is the biological toxic factor of Pb (the value is 5) (Sheykhi and Moore, 2013). Five classes of potential ecological risk were adopted according to the $E_r$ values: low ecological risk ($E_r < 40$), moderate ecological risk ($40 \le E_r < 80$), considerable ecological risk ($80 \le E_r < 160$), high ecological risk ($160 \le E_r < 320$), very high ecological risk ($320 \le E_r$).

The calculated $I_{geo}$ values of Pb and Sr, and $E_r$ values of Pb in the surface sediments of Jiulong River were shown in Fig. 3. Supported by the $I_{geo}$ classification, the mean $I_{geo}$ of Pb was 0.7, with 9.4% samples presenting non-contamination ($I_{geo}<0$), 71.7% samples presenting slight contamination ($0 \le I_{geo}<1$) and 11.3% samples presenting moderate contamination ($1 \le I_{geo}<2$). Pb presented strong contamination at sites 2 and 3, which might be associated with the surrounding deposits or sewage treatment plants. The mean $I_{geo}$ of Sr was 0.4, with 35.8% samples presenting non-contamination ($I_{geo}<0$) and 52.8% samples presenting slight contamination ($0<I_{geo}<1$). Supported by the $E_r$ classification, Pb had an average $E_r$ of 15.9, with 96.2% of the samples showing low ecological risk in the study area. Pb had considerable ecological risk ($80<E_r < 160$) at sites 2 and 3. In summary, Pb and Sr presented slightly contaminated, and Pb had low ecological risk at most sampling sites for the surface sediments of Jiulong River.

### 3.3. Pb isotopic tracing

The ranges of $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ in the surface sediments of Jiulong River following total digestion were 1.1590–1.1924 and 2.0849–2.1159, respectively. They were relatively similar to the ratios of coal combustion (1.1498 ± 0.0034 and 2.1252 ± 0.0062), Fujian Pb-Zn deposit (1.1796 ± 0.0033 and 2.1025 ± 0.0028) and parent material (1.1956 ± 0.0041 and 2.0787 ± 0.0075), while clearly distinct from vehicle exhaust (1.1301 ± 0.0166 and 2.0692 ± 0.0420), indicating that vehicle exhaust could not be the major Pb source to surface sediments.

Plot of $^{206}Pb/^{207}Pb$ vs 1/[Pb] can be used to identify the characteristics of lead sources (Álvarez-Iglesias et al., 2012; N'Guessan et al., 2009). It was found that $^{206}Pb/^{207}Pb$ was not well related to 1/[Pb] ($r^2 = 0.0025$, Fig. 4(a)), suggesting that Pb variations were controlled by more than two sources with different lead isotopic compositions.

$^{208}Pb/^{206}Pb$ vs $^{206}Pb/^{207}Pb$ in the surface sediments and some potential sources (coal combustion, Fujian Pb–Zn deposit, vehicle exhaust and parent material) were plotted in Fig. 5(a). As shown in Fig. 5(a), isotopic ratios of total Pb were relatively similar to the ratios of coal combustion, Fujian Pb-Zn deposit and parent material, but rather away from vehicle exhaust. This result suggested that the total Pb accumulated in the surface sediments of Jiulong River was mainly from natural source and anthropogenic sources (coal combustion and Fujian Pb–Zn deposit), while vehicle exhaust was not the main source of Pb contamination in the sediments.

A three-end-member model was employed to analyze the contribution rates of parent material, coal combustion and Fujian Pb-Zn deposit to total Pb in the surface sediments (Cheng and Hu, 2010). The contribution rate of each source was calculated using Formulae (3)–(5).

$$f_1 + f_2 + f_3 = 100\% \tag{3}$$

$$f_1\left(\frac{^{206}Pb}{^{207}Pb}\right)_1 + f_2\left(\frac{^{206}Pb}{^{207}Pb}\right)_2 + f_3\left(\frac{^{206}Pb}{^{207}Pb}\right)_3 = \left(\frac{^{206}Pb}{^{207}Pb}\right)_s \tag{4}$$

$$f_1\left(\frac{^{208}Pb}{^{206}Pb}\right)_1 + f_2\left(\frac{^{208}Pb}{^{206}Pb}\right)_2 + f_3\left(\frac{^{208}Pb}{^{206}Pb}\right)_3 = \left(\frac{^{208}Pb}{^{206}Pb}\right)_s \tag{5}$$

Where, the subscript s, 1, 2 and 3 represent the samples, parent material, coal combustion and Fujian Pb-Zn deposit, respectively, and $f_1$, $f_2$ and $f_3$ are their relative contribution rates, respectively. Thus, the values of $(^{206}Pb/^{207}Pb)_1$, $(^{206}Pb/^{207}Pb)_2$ and $(^{206}Pb/^{207}Pb)_3$ were 1.1956 ± 0.0041, 1.1498 ± 0.0034 and 1.1796 ± 0.0033, respectively. The values of $(^{208}Pb/^{206}Pb)_1$, $(^{208}Pb/^{206}Pb)_2$ and $(^{208}Pb/^{206}Pb)_3$ were 2.0787 ± 0.0075, 2.1252 ± 0.0062 and 2.1025 ± 0.0028, respectively. The contribution rates of natural source (parent material), coal combustion and Fujian Pb-Zn deposit calculated from the three-end-member model were shown in Table 1.

Overall, the average contribution rates of parent material, coal combustion and Fujian Pb-Zn deposit to total Pb in the surface

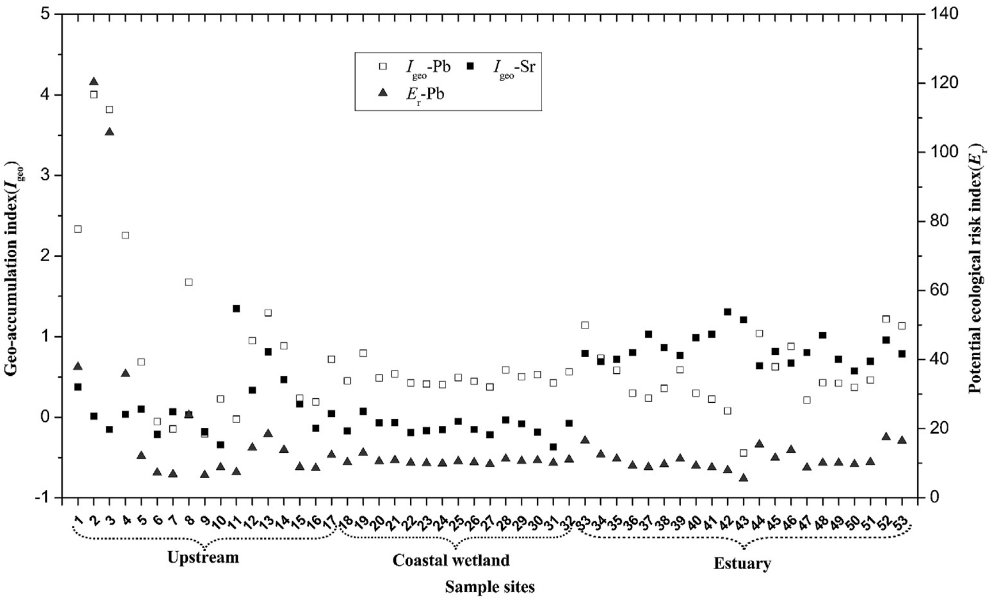

**Fig. 3.** Geo-accumulation index ($I_{geo}$) calculated from total Pb and Sr, and potential ecological risk index ($E_r$) calculated from total Pb.

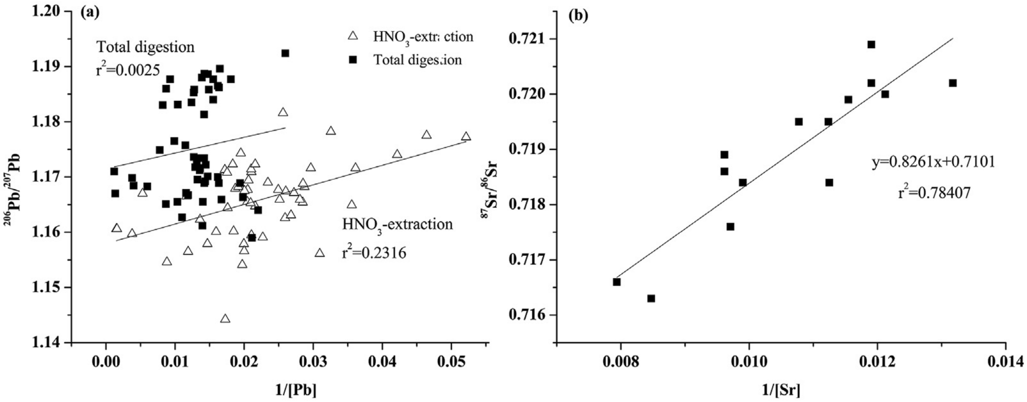

**Fig. 4.** Plot of isotopic compositions and concentrations in the surface sediments of Jiulong River (a) $^{206}$Pb/$^{207}$Pb vs 1/[Pb]; (b) $^{87}$Sr/$^{86}$Sr vs 1/[Sr].

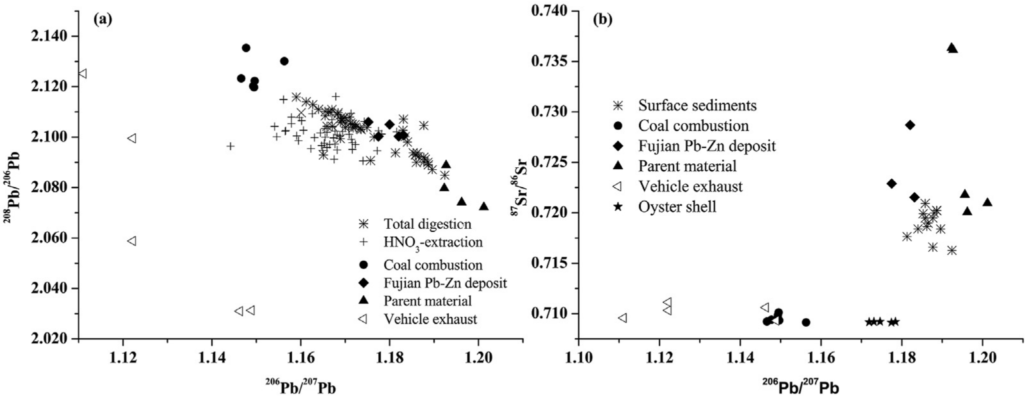

**Fig. 5.** Isotopic compositions in surface sediments of Jiulong River and potential sources (a) $^{208}$Pb/$^{206}$Pb vs $^{206}$Pb/$^{207}$Pb; (b) $^{87}$Sr/$^{86}$Sr vs $^{206}$Pb/$^{207}$Pb.

sediments were around 34.4%, 34.0% and 31.6%, respectively. Considering the variations of total Pb in the surface sediments, the average contribution rates of parent material, coal combustion and Fujian Pb-Zn deposit were 25.3%, 52.8% and 21.9% for Jiulong River upstream; 27.5%, 49.4% and 23.1% for coastal wetland; 46.7%, 7.8% and 45.5% for Jiulong River estuary, respectively.

### *3.4. Pb isotopic compositions in 0.5 mol/L $HNO_3$-extraction*

An average 62.9% of total Pb in the investigated surface sediment samples was extracted by 0.5 mol/L $HNO_3$. The ranges of $^{206}$Pb/$^{207}$Pb and $^{208}$Pb/$^{206}$Pb in the surface sediments of Jiulong River following 0.5 mol/L $HNO_3$-extraction were 1.1442–1.1816 and 2.0906–2.1161, respectively.

0.5 mol/L $HNO_3$-extraction had lower ratios of $^{206}$Pb/$^{207}$Pb than total digestion (1.1442–1.1816 and 1.1590–1.1924, respectively). As shown in Fig. 5(a), isotopic ratios of $HNO_3$-extraction Pb were closer to anthropogenic sources (coal combustion and Fujian Pb-Zn deposit) than total digestion. Generally, the $^{206}$Pb/$^{207}$Pb of anthropogenic source was lower than natural source (Komárek et al., 2008), the differences of $^{206}$Pb/$^{207}$Pb in total and acid-extractable phase indicated that Pb isotopic compositions in acid-extractable phase were more similar to anthropogenic source than total phase (Li et al., 2011). The correlation between $^{206}$Pb/$^{207}$Pb ratios and 1/[Pb] was more significant in dilute $HNO_3$-extraction ($r^2 = 0.2316$) than in total digestion ($r^2 = 0.0025$) (Fig. 4(a)). This result indicated that dilute $HNO_3$-extraction was more sensitive in identifying anthropogenic Pb sources than total digestion.

### *3.5. Sr isotopic tracing*

The $^{87}$Sr/$^{86}$Sr of the surface sediments from Jiulong River estuary and potential sources (coal combustion, Fujian Pb-Zn deposit, oyster shell, parent material and vehicle exhaust) were 0.7189 ± 0.0014, 0.7095 ± 0.0004, 0.7244 ± 0.0038, 0.7092 ± 0.0001, 0.7271 ± 0.0084 and 0.7102 ± 0.0008, respectively. Plot of $^{87}$Sr/$^{86}$Sr vs 1/[Sr] may be employed to identify the characteristics of Sr sources (Revel-Rolland et al., 2005). $^{87}$Sr/$^{86}$Sr vs 1/[Sr] in the surface sediments of Jiulong River estuary was plotted in Fig. 4(b). It was found that $^{87}$Sr/$^{86}$Sr of the surface sediments was well related to 1/[Sr] ($r^2 = 0.7841$), suggesting that Sr variations were controlled by one or a mixing of external sources with different Sr isotopic compositions.

$^{87}$Sr/$^{86}$Sr of external source was indicated on Y axis of Fig. 4(b) (N'Guessan et al., 2009). When 1/[Sr] tends to zero, the average $^{87}$Sr/$^{86}$Sr of external source was 0.7101. A two-end-member model was employed to analyze the contribution rates of external source and natural source (parent material). The contribution rate of each source was calculated using Formulae (6) And (7).

$$Sr_{anth}(\%) = \frac{(^{87}Sr/^{86}Sr)_{sample} - (^{87}Sr/^{86}Sr)_{natural}}{(^{87}Sr/^{86}Sr)_{external} - (^{87}Sr/^{86}Sr)_{natural}} \times 100 \quad (6)$$

$$Sr_{natural}(\%) = 100\% - Sr_{external}(\%) \quad (7)$$

According to above discussion, the values of $(^{87}Sr/^{86}Sr)_{external}$ and $(^{87}Sr/^{86}Sr)_{natural}$ were 0.7101 and 0.7271, respectively. The contribution rates of external source and natural source calculated

**Table 1**
Contribution rates of natural sources (parent material) and anthropogenic sources (coal combustion and Fujian Pb-Zn deposit) to total Pb in the surface sediments from Jiulong River.

| Sites | Natural sources (%) | Anthropogenic sources (%) | | Sites | Natural sources (%) | Anthropogenic sources (%) | |
|---|---|---|---|---|---|---|---|
| | Parent material | Coal combustion | Pb-Zn deposit | | Parent material | Coal combustion | Pb-Zn deposit |
| 1 | 17.1 | 43.5 | 39.4 | 28 | 32.9 | 39.1 | 28.0 |
| 2 | 8.0 | 34.3 | 57.7 | 29 | 28.3 | 37.2 | 34.5 |
| 3 | 7.7 | 48.0 | 44.3 | 30 | 21.5 | 47.0 | 31.5 |
| 4 | 9.1 | 43.9 | 47.0 | 31 | 25.2 | 51.1 | 23.7 |
| 5 | 18.7 | 55.2 | 26.1 | 32 | 38.2 | 48.3 | 13.5 |
| 6 | 19.5 | 57.0 | 23.5 | 33 | 31.9 | 68.1 | 0.0 |
| 7 | 15.3 | 80.1 | 4.6 | 34 | 55.6 | 44.4 | 0.0 |
| 8 | 15.5 | 47.9 | 36.6 | 35 | 40.2 | 0.8 | 58.9 |
| 9 | 25.4 | 68.3 | 6.4 | 36 | 50.6 | 0.0 | 49.4 |
| 10 | 37.7 | 58.1 | 4.2 | 37 | 43.1 | 0.0 | 56.9 |
| 11 | 40.4 | 59.6 | 0.0 | 38 | 41.9 | 1.8 | 56.3 |
| 12 | 40.1 | 33.0 | 26.9 | 39 | 37.5 | 1.0 | 61.5 |
| 13 | 18.2 | 26.4 | 55.4 | 40 | 27.5 | 0.0 | 72.5 |
| 14 | 33.3 | 66.7 | 0.0 | 41 | 41.3 | 0.0 | 58.8 |
| 15 | 44.4 | 55.7 | 0.0 | 42 | 53.6 | 1.6 | 44.8 |
| 16 | 43.2 | 56.8 | 0.0 | 43 | 80.0 | 0.0 | 20.0 |
| 17 | 36.4 | 63.6 | 0.0 | 44 | 50.6 | 0.0 | 49.4 |
| 18 | 17.6 | 73.7 | 8.7 | 45 | 24.4 | 0.0 | 75.6 |
| 19 | 17.5 | 68.4 | 14.0 | 46 | 21.9 | 0.0 | 78.1 |
| 20 | 27.7 | 43.2 | 29.1 | 47 | 66.9 | 2.4 | 30.7 |
| 21 | 32.6 | 43.5 | 24.0 | 48 | 62.2 | 28.6 | 9.2 |
| 22 | 32.5 | 39.6 | 28.0 | 49 | 56.9 | 0.0 | 43.1 |
| 23 | 30.9 | 53.3 | 15.9 | 50 | 56.3 | 0.0 | 43.8 |
| 24 | 25.7 | 40.0 | 34.4 | 51 | 52.5 | 0.0 | 47.5 |
| 25 | 26.0 | 43.6 | 30.4 | 52 | 21.3 | 0.0 | 78.8 |
| 26 | 22.8 | 61.6 | 15.6 | 53 | 64.9 | 13.8 | 21.3 |
| 27 | 33.6 | 51.7 | 14.7 | | | | |

from the two-end-member model were shown in Table 2. The average contribution rates of external source and natural source (parent material) to total Sr in the surface sediments of Jiulong River estuary were around 48.1% and 51.9%, respectively.

### 3.6. Combined Pb and Sr isotopic tracing

$^{87}Sr/^{86}Sr$ vs $^{206}Pb/^{207}Pb$ in surface sediments and some potential sources (coal combustion, Fujian Pb–Zn deposit, vehicle exhaust, oyster shell and parent material) was plotted in Fig. 5(b). As shown in Fig. 5(b), $^{206}Pb/^{207}Pb$ and $^{87}Sr/^{86}Sr$ of 14 surface sediments from Jiulong River estuary were close to parent material and Fujian Pb-Zn deposit, indicated that Pb and Sr accumulated in the surface sediments of Jiulong River estuary were mainly influenced by parent material and Fujian Pb-Zn deposit. The average $^{87}Sr/^{86}Sr$ of external source was 0.7101, it illustrated that Fujian Pb-Zn deposit was not the only external source. According to above discussion, vehicle exhaust and coal combustion wasn't the main sources of Pb in the sediments of Jiulong River estuary. According to 3.1 section, Sr concentrations were higher in the surface sediments of Jiulong River estuary, this result suggested that Sr might be influenced by seawater. The $^{87}Sr/^{86}Sr$ ratio of oyster shell was 0.7092 ± 0.0001 which representing marine source. These results illustrated that the Sr accumulated in the surface sediments of Jiulong River estuary was mainly from parent material, Fujian Pb-Zn deposit and marine source.

## 4. Conclusion

Pb and Sr concentrations and Pb isotopic compositions (both total and acid-extractable), and Sr isotopic compositions (total digestion) in fifty-three surface sediment samples from Jiulong River, Southeast China, were determined to trace the sources of Pb and Sr. The average concentrations of Pb and Sr were 110.9 mg/kg and 69.2 mg/kg, approximately 3.2 and 2.0 times of the local soil background values of 34.9 mg/kg and 34.0 mg/kg, respectively. The average calculated $I_{geo}$ value was 0.7 for total Pb and 0.4 for total Sr, indicating that surface sediments of Jiulong River were slight contamination by Pb and Sr. The average calculated $E_r$ value was 15.9 for total Pb, indicating that Pb had low ecological risk in most surface sediments of Jiulong River. 27.2%–85.2% (with the mean of 62.9%) of total Pb and 18.7%–72.8% (with the mean of 36.8%) of total Sr were extracted by 0.5 mol/L $HNO_3$ for the investigated surface sediment samples, indicating that Pb was more mobile and had higher risk to the ecological environment than Sr in surface sediments of Jiulong River.

**Table 2**
Contribution rates of external source and natural source to total Sr in the surface sediments from Jiulong River estuary.

| Sites | External source (%) | Natural source (%) | Sites | External source (%) | Natural source (%) |
|---|---|---|---|---|---|
| 35 | 36.4 | 63.6 | 42 | 61.9 | 38.1 |
| 36 | 44.9 | 55.1 | 43 | 63.8 | 36.3 |
| 37 | 47.9 | 52.2 | 47 | 51.3 | 48.7 |
| 38 | 44.9 | 55.1 | 48 | 55.7 | 44.3 |
| 39 | 42.3 | 57.7 | 49 | 40.6 | 59.4 |
| 40 | 51.2 | 48.8 | 50 | 40.5 | 59.5 |
| 41 | 49.8 | 50.2 | 51 | 41.9 | 58.1 |

The plots of $^{206}Pb/^{207}Pb$ vs 1/[Pb] and $^{208}Pb/^{206}Pb$ vs $^{206}Pb/^{207}Pb$ indicated that total Pb accumulated in the surface sediments of Jiulong River was mainly from parent material, coal combustion and Fujian Pb-Zn deposit, while vehicle exhaust was not the major source. A three-end-member model for Pb isotope was employed to analyze the contribution rates of three major sources to total Pb in the sediments. The mean contribution rates of parent material, coal combustion and Fujian Pb-Zn deposit to total Pb in the surface sediments were 34.4%, 34.0%, and 31.6%, respectively, suggesting coal combustion and Fujian Pb-Zn deposit were the major sources of anthropogenic Pb. Pb isotopic compositions in 0.5 mol/L $HNO_3$-extraction suggested that $HNO_3$-extraction was more sensitive in identifying anthropogenic Pb sources than total digestion. The plots of $^{87}Sr/^{86}Sr$ vs 1/[Sr] suggested that Sr in the surface sediments of Jiulong River estuary mainly derived from external source and natural source (parent material) with the contribution rates of around 48.1% and 51.9%, respectively, according to a two-end-member model. Combination of Pb and Sr isotopes illustrated that Sr accumulated in the surface sediments of Jiulong River estuary was mainly from parent material, Fujian Pb-Zn deposit and marine source.

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