Baseline

Heavy metal pollution and Pb isotopic tracing in the intertidal surface sediments of Quanzhou Bay, southeast coast of China

Ruilian Yu [a,*], Weifang Zhang [a], Gongren Hu [a,b], Chengqi Lin [a], Qiuli Yang [a]

[a] Department of Environmental Science and Engineering, Huaqiao University, Xiamen, China
[b] State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang, china

ARTICLE INFO

ABSTRACT

Concentrations of 16 heavy metals and Pb isotopic ratios in the intertidal surface sediments of Quanzhou Bay were determined to study the pollution level of heavy metals and the sources of Pb. The results showed that most concentrations of Cd, Sn, Mn, Cu, Zn, Cr, Pb, Hg, Ni, Co, Cs, Fe and V were higher than the background values, while most concentrations of Ti, Sb and Sr were lower than the background values. The mean concentrations of Cu, Zn, Pb, Cr and Cd exceeded the first-grade criteria of Chinese marine sediment quality. The geo-accumulation indexes revealed that the sediments had been polluted by some heavy metals. The results of Pb isotopic tracing indicated that the total Pb in the sediments were mainly from parent material, industrial emission and vehicle exhaust with the mean contributions of 38.2%, 51.3% and 10.5%, respectively, calculated by a three-end-member model of Pb isotopic ratios.

With the rapid economic development and population growth, a large amount of industrial, agricultural wastewater and sewage has been discharged into various water bodies such as lakes, rivers and oceans, resulting in deterioration of the water environment (Mulligan et al., 2001). Among the substantial pollutants, heavy metals have been paid much attention due to their toxicity, non-biodegradation, persistence and bioaccumulation. Most heavy metals will rapidly deposit into sediment after being discharged into a body of water, and may release again to the water owing to the variation of environmental conditions such as the physical, chemical, biological processes and human activities (Beck et al., 2013). Therefore, sediment is the sink and the second source of heavy metals in water body. Pollution of heavy metals in sediment is a great risk for human health and has increasingly received public attention (Li et al., 2012).

It is essential to determine the source of pollution for investigating and mitigating the pollution. Isotopic measurement is superior to using pollutant concentration alone in tracing pollutant sources because isotope ratios are significantly more sensitive tracers than elemental concentrations (Aggarwal et al., 2008; Cheng and Hu, 2010). The analysis of Pb isotopic ratios has been proved a powerful tool for identifying Pb pollution sources and assessing the relative contributions (Balcaen et al., 2010; Chiaradia et al., 1997; Michael et al., 2008). There are four naturally stable isotopes of Pb: [204]Pb, [206]Pb, [207]Pb and [208]Pb. Among them, [204]Pb is the only non-radiogenic with a constant abundance, while the other three isotopes are derived from the

radioactive decay of [238]U to [206]Pb (decay half-time of the parent isotope $t_{1/2} = 4.468 \times 10^9$ years), [235]U to [207]Pb ($t_{1/2} = 0.704 \times 10^9$ years) and [232]Th to [208]Pb ($t_{1/2} = 1.401 \times 10^{10}$ years) (Álvarez-Iglesias et al., 2012; Cheng and Hu, 2010; Larsen et al., 2012; Townsend and Seen, 2012). Pb isotopic fractionation does not occur in industrial and environmental processes, in other words, industrial and environmental processes hardly change the isotopic composition of Pb after it is released into the environment from the original ore (Cheng and Hu, 2010). Materials from different sources possess different radiogenic Pb isotopes, hence the radiogenic Pb isotope ratios can be used as a fingerprint to trace the different sources of Pb in the given environment (Ip et al., 2007; Li et al., 2012; Sun et al., 2011).

As the famous starting place of the Maritime Silk Road in ancient China, Quanzhou Bay is located in the southeast of Fujian province and to the west of Taiwan Straits. It is a semi-enclosed bay with its mouth opening towards the Taiwan Straits, with a greatest water depth of 25 m, a mouth width of 8.9 km, a total area of 136.42 km^2 and an intertidal area of 89.80 km^2 (Yu et al., 2008). The bay is adjacent to some intensely industrialized cities such as Quanzhou city, Jinjiang city, Shishi city and Hui'an county. There are two considerable rivers entering into the bay, namely Jinjiang River and Luoyang River. The intertidal zone of Quanzhou Bay has been polluted by heavy metals due to the rapid development of industry, agriculture, mining and aquatic breeding in the surrounding regions (Yu et al., 2008). In recent years, there have been several studies on heavy metal pollution in the sediments of Quanzhou Bay. These previous studies mainly focused on the distribution, pollution assessment and chemical speciation of heavy metals in sediments (Hu et al., 2013; Li et al., 2010; Yu et al.,

* Corresponding author.

2008, 2010). However, the source analysis of heavy metals in the sediments of Quanzhou Bay has seldom been reported to date. How to identify the sources of pollutants is an important issue in controlling the environment pollution. The aims of this study were to investigate the level of 16 heavy metals (Ti, V, Cr, Mn, Co, Ni, Cu, Zn, Cd, Pb, Fe, Cs, Sb, Sn and Sr and Hg) in the intertidal surface sediments of Quanzhou Bay, to evaluate the pollution degree of heavy metals using geo-accumulation index method, and to discuss Pb sources based on the Pb isotopic tracing technology.

In December 2011, 41 surface sediments (0–5 cm) were collected in the intertidal zone of Quanzhou Bay (Fig. 1). The sampled sediments were stored in clean sealed plastic bags and kept frozen at −20 °C prior to pretreatment. In the laboratory, the sediment samples were defrosted and air-dried in a clean environment. When the sediments were semi-dry, a clean glass bottle was used to crush the sediments. Then, the sediment samples were put into an oven and dried at 35 ± 2 °C to a constant weight. The dry sediment samples were ground with an agate pestle and mortar, then sieved with a 63 μm nylon sieve. The samples under the sieve (<63 μm) were kept in sealed plastic vessels at 4 °C for further analysis (Horowitz and Elrick, 1987).

For each sediment sample, 0.1000 g dry sediment was put into a 50-mL Teflon vessel with 6 mL HNO_3, 2 mL HCl, 2 mL H_2O_2, and 1 mL HF, digested at 180 °C in a closed system for 12 h. After digestion, the completely dissolved sample was diluted with deionized water to 100 mL for further analysis. For each batch of digestion procedure, a reagent blank and a sediment reference material, GBW07314, issued by the State Oceanographic Administration of China, were processed with the same digestion procedure.

Concentrations of Ti, V, Cr, Mn, Co, Ni, Cu, Zn, Cd, Pb, Fe, Cs, Sb, Sn and Sr in the digestion solutions were determined by inductively coupled plasma-mass spectrometry (ICP-MS) (ELAN9000, Perkin-Elmer, USA) with the detection limits of 0.001–0.098 μg L^{-1}, while Hg was determined with an automatic mercury analyzer RA-3 (NIC, Japan) with the detection limit of 0.009 μg L^{-1}. Background correction and matrix interference were monitored throughout the analyses. All the solutions were analyzed in triplicates. The analytical precisions were better than 10%. The analytical results of the measured metals showed a good agreement between the reference and the analytical values for the reference material GBW07314 with the recovery range of 87%–106%.

The analysis of Pb isotopic composition was conducted in the clean laboratory of Beijing Research Institute of Uranium Geology. Sample preparation including sample digestion, separation and purification was processed according to the analytical procedures of Chinese geological mineral industry standard DZ/T 0184.12-1997. Pb isotopic composition was determined by thermal ionization mass spectrometry (VG354, VG Instruments, UK). The reference material (NBS981, National Bureau of Standards, USA) was used for the quality control in the analysis process of Pb isotopic ratios. The $^{208}Pb/^{206}Pb$, $^{207}Pb/^{206}Pb$ and $^{207}Pb/^{204}Pb$ of the reference material NBS981 were 2.1681 ± 0.0008, 0.91462 ± 0.00037 and 15.4910 ± 0.0064, respectively. In this study, 28 sediment samples were measured for Pb isotopic ratios with the relative standard deviations of less than 0.05%. The Pb isotopic compositions of local potential-source samples including parent materials, industrial emissions (industrial sludge in this study), coal and vehicle exhaust were cited from Hu et al. (2013).

Guaranteed reagents were used in the concentration determination of heavy metals, and MOS reagents were used in the analysis of Pb isotopic ratios. Normal precautions for the analyses were observed throughout. Double deionized water from a MILLI-Q system was used for preparing the solutions and dilutions. All the glassware and the Teflon vessels used in the study were previously soaked overnight with 20% HNO_3 and then rinsed thoroughly with deionized water. The data were processed using Excel 2007 and Origin 8.0 software packages. ArcGIS 10.2 was used to draw the map of sampling sites.

As shown in Table 1, the concentrations of heavy metals in the intertidal surface sediments of Quanzhou Bay were different at distinct sampling sites that might be attributed to the possible pollution source inputs. The concentration ranges of Ti, V, Cr, Mn, Co, Ni, Cu, Zn, Cd, Pb, Fe, Cs, Sb, Sn, Sr and Hg were 2005–4860, 62.96–100.80, 52.76–165.9, 697–1857, 9.44–15.04, 16.22–45.72, 24.82–160.6, 120.4–324.5, 0.280–1.155, 37.03–93.19, 33,200–42,561, 5.81–9.82, 0.308–1.930, 7.39–25.91, 30.76–185.2 and 0.107–0.350 mg kg^{-1}, respectively, with the mean concentrations of 3431, 83.75, 84.72, 1295, 11.93, 26.77, 60.81, 186.7, 0.639, 66.98, 38,455, 7.37, 0.886, 12.59, 88.53 and 0.107 mg kg^{-1}, respectively. It should be noted that 100% samples for Cr, Mn, Cu, Zn, Cd, Sn and Hg, 97.6% samples for Co, Pb and Fe, 95.1% samples for Ni, 85.4% samples for Cs, 73.2% samples for V, 31.7% samples for Sb, 12.2% samples for Ti and 2.4% samples for Sr exceeded the background values. The mean concentrations of Cd, Sn, Mn, Cu, Zn, Cr, Pb, Hg, Ni, Co, Cs, Fe
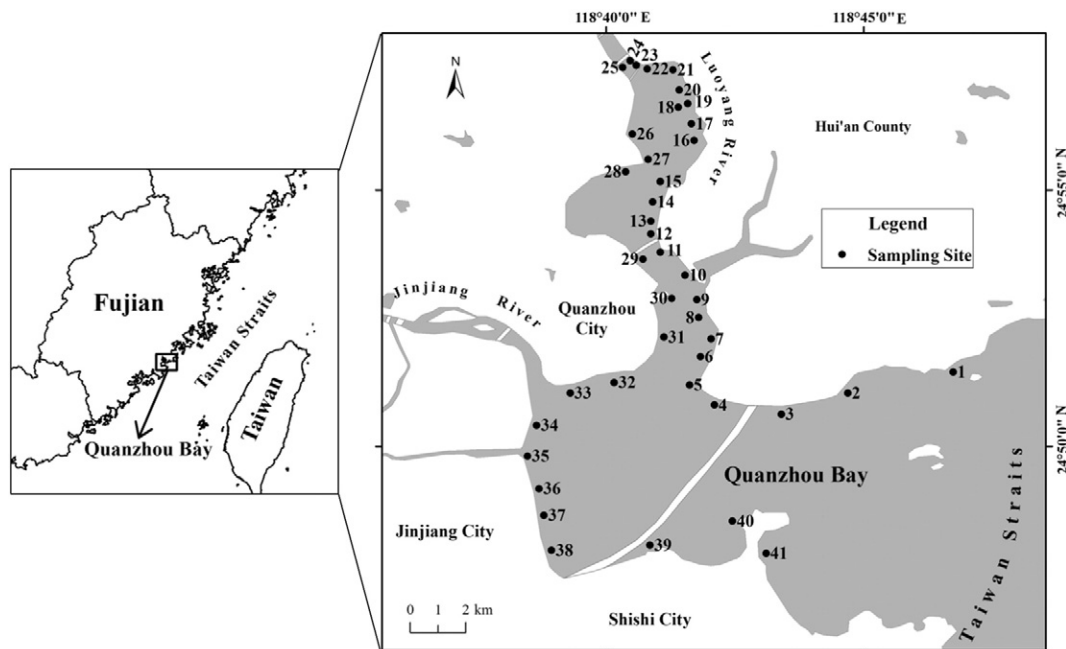

Fig. 1. Map of sampling sites.

Table 1
Concentrations (mg kg^{-1}) of heavy metals in the intertidal surface sediments of Quanzhou Bay.

Site	Ti	V	Cr	Mn	Co	Ni	Cu	Zn	Cd	Pb	Fe	Cs	Sb	Sn	Sr	Hg
1	3768	66.24	79.88	1270	10.91	23.87	40.47	134.3	0.590	57.76	35,900	7.40	0.556	19.72	93.40	0.035
2	2756	96.78	77.08	989	10.71	24.71	43.71	135.0	0.858	41.92	35,600	7.24	1.458	24.32	99.00	0.080
3	2791	70.42	131.4	903	9.44	27.91	37.31	164.3	0.824	59.64	33,200	6.77	1.336	18.70	105.0	0.273
4	2005	91.32	165.9	1109	10.33	22.11	32.81	149.7	0.740	59.86	35,800	5.83	1.814	21.64	83.76	0.350
5	2942	62.96	82.60	1161	10.14	17.41	36.28	164.9	0.770	59.26	38,092	5.88	0.561	7.74	96.54	0.072
6	3119	87.38	87.37	1223	10.92	20.61	50.28	218.3	0.872	64.02	40,042	6.76	1.190	12.50	95.50	0.100
7	3299	77.67	54.91	1857	10.24	24.15	25.93	120.4	0.307	49.86	42,561	6.78	0.500	7.54	185.2	0.082
8	2999	80.24	118.3	1059	10.59	21.57	52.94	243.9	0.690	73.96	40,692	6.68	0.616	8.47	84.58	0.068
9	3096	79.88	97.17	1327	10.99	23.03	56.12	190.1	0.631	66.30	41,732	6.48	0.681	9.03	98.28	0.079
10	3929	76.26	66.96	1255	10.67	30.08	54.26	172.5	0.681	72.26	38,501	7.95	0.645	12.20	88.40	0.161
11	3244	76.00	96.57	1311	10.83	22.81	81.60	174.1	0.721	90.49	38,222	6.52	0.842	10.58	88.44	0.096
12	3153	94.35	71.63	1081	14.07	32.90	44.62	191.1	0.553	77.02	40,665	8.60	0.770	11.36	83.80	0.099
13	4860	95.43	65.90	1384	13.23	30.64	40.58	170.3	0.440	79.06	36,306	8.82	0.874	10.11	80.01	0.056
14	3153	84.90	113.4	1402	10.77	22.67	72.64	222.9	0.736	72.88	39,002	6.66	0.665	9.73	74.96	0.122
15	4178	90.54	63.11	1445	13.44	29.34	38.21	179.9	0.459	71.99	39,777	8.06	0.708	9.51	88.31	0.030
16	2724	65.96	114.9	1457	10.63	20.61	41.78	237.9	0.721	73.98	38,612	6.10	0.726	10.84	98.30	0.080
17	3153	90.27	63.41	1492	13.42	29.98	37.77	185.6	0.458	71.85	37,565	8.23	0.636	10.24	79.68	0.093
18	3200	88.16	98.27	1387	11.18	20.59	87.94	158.9	0.749	72.36	41,602	6.97	0.446	9.41	80.13	0.053
19	3299	80.71	54.71	1691	12.05	26.16	43.89	173.5	0.526	74.57	40,714	7.57	0.671	10.92	73.91	0.086
20	2962	90.12	101.0	1467	11.48	24.21	160.6	310.9	0.671	64.95	40,042	7.32	0.308	10.94	80.98	0.106
21	3910	85.10	52.76	1435	13.02	23.59	27.24	142.9	0.381	58.66	36,950	6.81	0.532	7.39	92.55	0.058
22	2910	94.70	98.87	1606	12.04	27.21	125.6	160.3	0.570	64.70	41,602	7.65	0.692	10.17	77.52	0.076
23	3014	91.34	64.97	1603	13.98	30.69	38.71	184.0	0.485	78.30	36,857	8.62	0.685	10.44	77.94	0.309
24	4389	100.80	58.90	1311	14.43	30.71	118.0	159.0	0.431	63.84	41,702	8.05	1.233	14.23	81.35	0.086
25	3416	91.37	59.50	1662	12.74	29.11	32.92	157.8	0.376	70.33	38,747	8.61	0.643	8.87	71.12	0.168
26	4623	89.22	62.19	1420	13.43	26.63	38.10	177.0	0.447	72.46	37,520	8.05	0.646	9.77	75.71	0.222
27	3013	71.18	81.62	1222	10.70	17.03	67.36	224.3	0.683	72.64	39,392	6.00	0.777	15.10	86.00	0.066
28	4853	88.15	63.48	1081	13.14	30.68	37.89	185.6	0.485	75.56	38,856	8.07	0.701	9.97	75.68	0.098
29	2532	84.70	87.67	1436	10.43	21.59	87.62	240.9	0.703	90.96	38,612	5.81	0.677	10.23	78.16	0.101
30	3078	72.04	130.2	1656	10.71	24.25	55.94	324.5	1.061	68.46	40,302	7.22	0.599	11.41	84.79	0.119
31	3082	81.66	85.87	1431	12.67	24.19	41.20	218.9	0.738	61.08	39,392	7.23	0.569	10.98	83.01	0.103
32	4532	87.22	65.46	965	14.90	28.86	37.55	193.7	1.155	93.19	36,891	8.19	0.847	14.43	76.16	0.153
33	3658	70.06	89.77	1008	10.26	25.19	38.56	165.1	0.831	60.64	36,921	6.34	0.668	12.64	162.4	0.101
34	4014	83.14	103.3	1185	12.18	45.72	80.34	193.5	0.570	62.11	37,200	8.70	1.687	9.29	92.81	0.011
35	3087	82.64	59.70	1102	15.04	20.79	90.27	198.9	0.890	64.74	39,200	6.75	1.192	10.16	30.76	0.029
36	2088	82.64	87.03	1108	11.97	38.49	111.4	182.3	0.530	62.20	38,600	8.47	1.281	10.51	95.00	0.099
37	3906	84.00	79.27	1085	11.41	36.11	78.30	190.1	0.730	63.44	40,400	8.70	1.930	15.14	83.50	0.082
38	4086	96.15	82.57	697	13.86	38.38	94.01	213.2	0.840	52.13	35,600	9.82	1.042	21.33	123.20	0.123
39	3990	83.07	70.63	930	11.90	34.90	119.7	164.9	0.430	56.91	34,600	8.64	1.272	8.96	100.4	0.086
40	3763	79.14	74.52	1222	12.27	31.92	67.83	135.4	0.580	62.73	37,800	6.05	1.014	23.76	52.00	0.072
41	4082	89.96	110.7	1658	11.83	16.22	24.82	146.5	0.280	37.03	34,900	5.96	1.616	25.91	71.50	0.121
Min	2005	62.96	52.76	697	9.44	16.22	24.82	120.4	0.280	37.03	33,200	5.81	0.308	7.39	30.76	0.107
Max	4860	100.8	165.9	1857	15.04	45.72	160.6	324.5	1.155	93.19	42,561	9.82	1.930	25.91	185.2	0.350
Mean	3431	83.75	84.72	1295	11.93	26.77	60.81	186.7	0.639	66.98	38,455	7.37	0.886	12.59	88.53	0.107
S.D.	687	9.16	24.68	253	1.46	6.26	31.96	42.52	0.190	11.49	2196	1.03	0.40	4.87	24.43	0.070
BG[a]	4200	79.70	40.70	507	9.48	17.40	22.40	83.6	0.060	39.00	34,000	6.30	0.960	3.40	160.0	0.063
Previous data[b]	–	–	82.0	–	–	33.4	71.4	179.6	0.59	67.7	–	–	–	–	–	0.40
Shantou Bay[c]	–	–	53.56	599	9.48	22.95	44.00	153.28	0.670	51.63	–	–	–	–	–	–
First-grade criteria[d]	–	–	80	–	–	–	35	150	0.5	60	–	–	–	–	–	0.20

"–" means no available compared data;
[a] Background values from Liu (1995) and Chi and Yan (2007).
[b] Previous observed data from Yu et al. (2008).
[c] Values from Qiao et al. (2013).
[d] Criteria in Chinese national standard—Marine Sediment Quality (GB 18668-2002).

and V were 965.0%, 270.3%, 175.1%, 171.5%, 123.3%, 108.2%, 71.7%, 69.8%, 53.8%, 25.8%, 17.0%, 13.1% and 5.1% higher than their background values, respectively, while the mean concentrations of Ti, Sb and Sr were lower than their background values. Compared with the previous investigated data in the same area (Yu et al., 2008), although the numbers of heavy metals and sampling sites were both larger in this study, the mean concentrations of Hg, Cu and Ni obviously decreased in this study, while the mean concentrations of Pb, Cr, Zn and Cd seldom changed. The mean concentrations of Cr, Mn, Co, Ni, Cu, Zn and Pb in this study were higher than those in Shantou Bay of China (Qiao et al., 2013), while Cd showed the same level in the two study areas.

According to the marine function regionalization of Fujian province and Quanzhou city, the sediments of this study area should meet the first-grade criteria of the Chinese national standard—Marine Sediment Quality GB 18668-2002 (Table 1). However, the mean concentrations of Cu, Zn, Pb, Cd and Cr exceeded the first-grade criteria of Chinese

marine sediment quality with the sample exceeding rates of 87.8%, 85.4%, 78.0%, 70.7% and 51.2%, respectively. The mean concentration of Hg met the first-grade criterion of the national standard with the sample exceeding rate of 9.8%. In short, the intertidal surface sediments of Quanzhou Bay had been polluted by some heavy metals, which might be related to the various anthropogenic activities.

Geo-accumulation index (I_{geo}), first proposed by Müller (1969), was employed to evaluate the pollution degree of heavy metals in the sediment. I_{geo} can be calculated by the following formula.

$$I_{geo} = \log_2[C_i/(1.5B_i)]$$

where, C_i and B_i are respectively the measured and the background concentrations of the examined metal i. Background concentrations of metals in the coastal region of Fujian province and the stream sediment in China (Sb, Sn, Sr, Cs) were used in this study (Table 1). 1.5 is the

background matrix correction factor due to lithogenic effects. According to the I_{geo} values, the pollution level of metal elements can be divided into 7 classes: class 0 (unpolluted) with $I_{geo} < 0$; class 1 (unpolluted to moderately polluted) with $0 \le I_{geo} < 1$; class 2 (moderately polluted) with $1 \le I_{geo} < 2$; class 3 (moderately to strongly polluted) with $2 \le I_{geo} < 3$; class 4 (strongly polluted) with $3 \le I_{geo} < 4$; class 5 (strongly to extremely polluted) with $4 \le I_{geo} < 5$; and Class 6 (extremely polluted) with $I_{geo} \ge 5$.

The calculated I_{geo} values of the studied heavy metals in this study were shown in Fig. 2. Most I_{geo} values of Cd fell in class 3, describing that Cd pollution was considerably serious in the intertidal zone of Quanzhou Bay. Most I_{geo} values of Sn fell in class 2, indicating moderate pollution. Most I_{geo} values of Cr, Mn, Cu, Zn and Pb fell in class 1, suggesting slightly to moderately polluted by these elements. Most I_{geo} values of Ni fell in class 0 and class 1, indicating unpollution to moderate pollution. It was worth noting that the I_{geo} values of Hg varied greatly, showing the obvious spatial difference, although most I_{geo} values of Hg also fell in class 0 and class 1. Most I_{geo} values of Ti, V, Fe, Sr, Cs, Co and Sb fell in class 0, indicating unpolluted by these elements. Based on the mean I_{geo} values, the intertidal surface sediments of Quanzhou Bay were enriched for the studied heavy metals in the order of Cd > Sn > Mn > Cu > Zn > Cr > Pb > Hg > Ni > Co > Cs > Fe > V > Sb > Ti > Sr.

Pb isotope ratios in the intertidal surface sediments were summarized in Table 2. The ranges of $^{208}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{206}Pb/^{204}Pb$ were 37.981–38.844, 15.361–16.601 and 18.152–18.581, respectively. The low $^{206}Pb/^{204}Pb$ (17.887) was the characteristics of local coal-fired Pb (Hu et al., 2013), indicating that the Pb in the studied sediments was less influenced by local fired coal.

Plot of $^{207}Pb/^{206}Pb$ vs 1/Pb can be used to identify the characteristics of Pb source (Álvarez-Iglesias et al., 2012; N'Guessan et al., 2009; Peng et al., 2011). There was no good linear correlation between $^{207}Pb/^{206}Pb$ and 1/Pb ($r^2 = 0.0053$, Fig. 3(a)) in the sediments, suggesting more than one significant anthropogenic sources in the intertidal surface sediments of Quanzhou Bay besides the natural sources. No single linear correlation was found between $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{(206+207)}Pb$ ($r^2 = 0.1685$) in the sediments, suggesting a mixture of more than two components with different Pb isotopic compositions. As shown in Fig. 3(b), the Pb isotope ratios in the sediments were near those in some industrial emissions and parent materials, indicating that industrial emissions and parent materials were the main sources of Pb in the sediments. Although the Pb isotopic ratios

Table 2
Pb isotope ratios in the intertidal surface sediments of Quanzhou Bay.

| Site	$^{208}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{206}Pb/^{204}Pb$	$^{206}Pb/^{207}Pb$
4	38.068	16.321	18.431	1.170
6	38.061	16.268	18.422	1.171
8	38.159	16.341	18.459	1.167
9	38.122	16.189	18.436	1.175
10	38.120	16.162	18.429	1.185
12	38.787	15.636	18.564	1.187
13	38.352	16.462	18.576	1.172
14	38.140	15.717	18.288	1.183
15	38.069	15.734	18.290	1.186
16	38.112	15.905	18.330	1.177
18	38.271	16.501	18.570	1.171
19	38.319	16.484	18.581	1.172
20	37.981	15.361	18.152	1.186
22	38.039	15.393	18.165	1.187
23	38.113	15.528	18.244	1.188
24	38.716	15.601	18.561	1.190
25	38.257	16.459	18.578	1.173
30	38.788	15.644	18.562	1.187
31	38.103	16.031	18.438	1.178
33	38.081	15.950	18.352	1.178
34	38.781	15.639	18.539	1.186
35	38.763	15.629	18.530	1.185
36	38.401	16.601	18.534	1.157
37	38.408	15.501	18.372	1.185
38	38.562	15.602	18.405	1.180
39	38.703	15.601	18.504	1.186
40	38.844	15.640	18.561	1.187
Mean	38.354	15.913	18.444	1.180

in the vehicle exhaust were quite scattering, the Pb isotopic ratios in some sediments were close to those in the vehicle exhaust. Thus, we could deem that the contribution of vehicle exhaust to the Pb in the sediments should not be ignored. The Pb isotope signature of local fired coal was relatively farther from those of the surface sediments, suggesting that the Pb in the sediments were less affected by the coal combustion. These results suggested that the Pb in the intertidal surface sediments of Quanzhou Bay might result from natural processes of weathering and transport of bedrocks, as well as from a range of anthropogenic activities, e.g. industrial emissions and vehicle exhaust.

Based on the above discussion that parent material, industrial emission and vehicle exhaust were the three major sources of Pb in the sediments, a three-end-member model could be used to calculate the contributions of parent material (f_1), industrial emission (f_2) and vehicle exhaust (f_3) to total Pb in the sediments. The calculation formulae are as follows (Li et al., 2011; Monna et al., 2000).

$$f_1 + f_2 + f_3 = 1$$
$$\frac{f_1 \times C_s}{C_1} + \frac{f_2 \times C_s}{C_2} + \frac{f_3 \times C_s}{C_3} = 1$$
$$f_1 \times R_1 + f_2 \times R_2 + f_3 \times R_3 = R_s$$

where, C_1, C_2 and C_3 are the mean total Pb concentrations of natural background sediment (26.64 $mg \cdot kg^{-1}$), industrial emission (6681.52 $mg \cdot kg^{-1}$) and vehicle exhaust (2379.53 $mg \cdot kg^{-1}$), respectively (Hu et al., 2013). R_1, R_2 and R_3 are the mean $^{206}Pb/^{207}Pb$ ratios of natural background sediment (1.201), industrial emission (1.170) and vehicle exhaust (1.130), respectively. C_s and R_s are the measured total Pb concentration and the $^{206}Pb/^{207}Pb$ ratio of each sediment sample.

The calculated contributions of parent material, industrial emission and vehicle exhaust to total Pb in the sediments were shown in Table 3. The contribution ranges of parent material, industrial emission and vehicle exhaust were 30.0%–48.5%, 8.4%–66.6% and 0%–58.2%, respectively, with the mean values of 38.2%, 51.3% and 10.5%, respectively. In the southwest of Quanzhou Bay, where there are many manufacturing
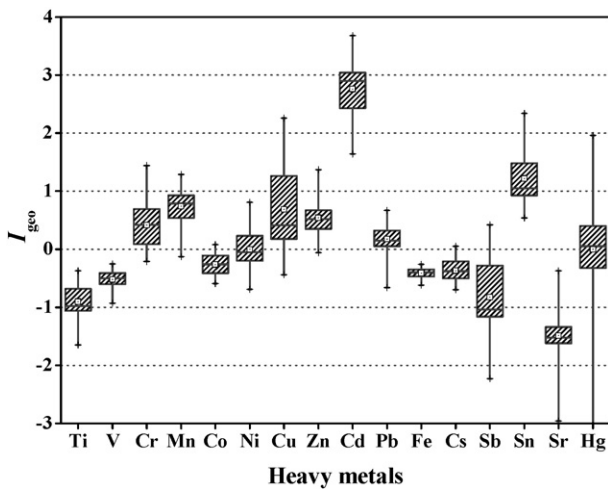
Fig. 2. Box variation plots of geo-accumulation index of the selected heavy metals in the sediments. The box represents the 25th to 75th percentiles, □ represents average values, + represents variation ranges of max and min values.
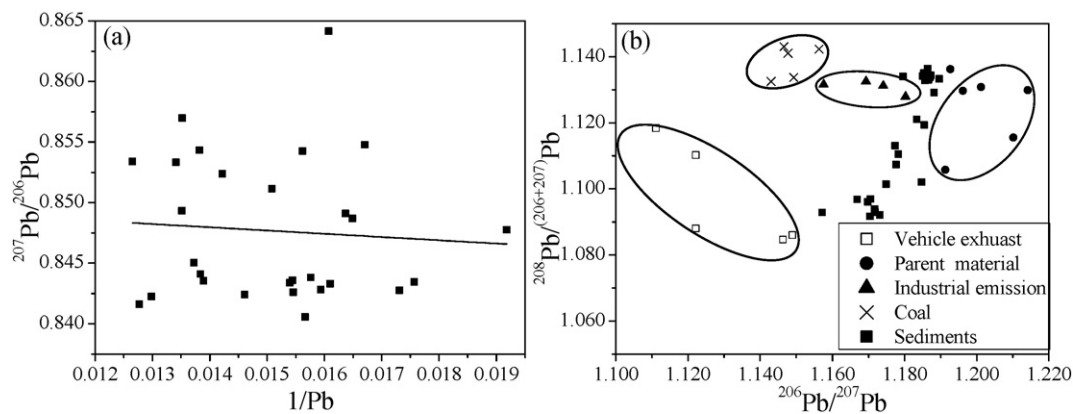
Fig. 3. Plots of ^{207}Pb/^{206}Pb versus 1/Pb (a) and ^{208}Pb/$^{(206+207)}$Pb versus ^{206}Pb/^{207}Pb (b) in the intertidal surface sediments of Quanzhou Bay and the known sources.

factories in Shishi city and Jinjiang city, the industrial emission was the predominant Pb source. By contrast, in the northern area of Quanzhou Bay, the source of Pb pollution was more complicated but the industrial emission was still the major anthropogenic Pb contributor.

Acknowledgments

Table 3
Contributions of potential sources to total Pb in the intertidal surface sediments of Quanzhou Bay (%).

Site	Parent material	Industrial emissions	Vehicle exhaust
1	45.9	54.1	0.0
4	39.2	29.8	31.0
6	36.8	35.8	27.4
8	30.5	37.7	31.8
9	37.0	46.2	16.8
10	36.6	63.4	0.0
12	34.0	66.0	0.0
13	30.0	50.7	19.2
14	36.4	63.6	0.0
15	36.7	63.3	0.0
16	34.0	57.6	8.3
18	32.4	43.3	24.3
19	31.9	47.7	20.4
20	40.8	59.2	0.0
22	40.8	59.2	0.0
23	33.4	66.6	0.0
24	41.2	58.8	0.0
25	34.3	46.7	19.0
30	38.5	61.5	0.0
31	41.0	46.0	12.9
33	41.5	46.7	11.8
34	42.7	57.3	0.0
35	40.9	59.1	0.0
36	33.4	8.4	58.2
37	41.8	58.2	0.0
38	48.5	37.7	13.9
39	46.7	53.3	0.0
40	42.2	57.8	0.0
Mean	38.2	51.3	10.5

References

Aggarwal, J., Habicht-Mauche, J., Juarez, C., 2008. Application of heavy stable isotopes in forensic isotope geochemistry: a review. Appl. Geochem. 23, 2658–2666. http://dx.doi.org/10.1016/j.apgeochem.2008.05.016.

Álvarez-Iglesias, P., Rubio, B., Millos, J., 2012. Isotopic identification of natural vs. anthropogenic lead sources in marine sediments from the inner Ria de Vigo (NW Spain). Sci. Total Environ. 437, 22–35. http://dx.doi.org/10.1016/j.scitotenv.2012.07.063.

Balcaen, L., Moens, L, Vanhaecke, F., 2010. Determination of isotope ratios of metals (and metalloids) by means of inductively coupled plasma-mass spectrometry for provenancing purposes—a review. Spectrochim. Acta B At. Spectrosc. 65, 769–786. http://dx.doi.org/10.1016/j.sab.2010.06.005.

Beck, M., Böning, P., Schückel, U., Stiehl, T., Schnetger, B., Rullkötter, J., Brumsack, H., 2013. Consistent assessment of trace metal contamination in surface sediments and suspended particulate matter: a case study from the Jade Bay in NW Germany. Mar. Pollut. Bull. 70, 100–111. http://dx.doi.org/10.1016/j.marpolbul.2013.02.017.

Cheng, H.F., Hu, Y.A., 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.

Chi, Q.H., Yan, M.C., 2007. Applied Geochemistry Element Abundances Data Sheet. Geological Publishing House, Beijing.

Chiaradia, M., Chenhall, B.E., Depers, A.M., Gulson, B.L., Jones, B.G., 1997. Identification of historical lead sources in roof dusts and recent lake sediments from an industrialized area: indications from lead isotopes. Sci. Total Environ. 205, 107–128. http://dx.doi.org/10.1016/s0048-9697(97)00199-x.

Horowitz, A.J., Elrick, K.A., 1987. The relation of stream sediment surface area, grain size and composition to trace element chemistry. Appl. Geochem. 2, 437–451. http://dx.doi.org/10.1016/0883-2927(87)90027–8.

Hu, G.R., Yu, R.L., Zheng, Z.M., 2013. Application of stable lead isotopes in tracing heavy-metal pollution sources in the sediments. Acta Sci. Circumst. 33, 1326–1331. http://dx.doi.org/10.13671/j.hjkxxb.2013.05.032.

Ip, C., Li, X.D., Zhang, G., Wai, O., Li, Y.S., 2007. Trace metal distribution in sediments of the Pearl River Estuary and the surrounding coastal area, South China. Environ. Pollut. 147, 311–323. http://dx.doi.org/10.1016/j.envpol.2006.06.028.

Larsen, M.M., Blusztajn, J.S., Andersen, O., Dahllöf, I., 2012. Lead isotopes in marine surface sediments reveal historical use of leaded fuel. J. Environ. Monit. 14, 2893–2901. http://dx.doi.org/10.1039/c2em30579h.

Li, Y.H., Chen, J., Huang, C.B., Wang, A.J., Li, D.Y., 2010. Distribution patterns of heavy metals in surface sediments of the Quanzhou Bay and environmental quality assessment. Environ. Sci. 31, 931–938. http://dx.doi.org/10.13227/j.hjkx.2010.04.007.

Li, H.B., Yu, S., Li, G.L., Deng, H., 2012. Lead contamination and source in Shanghai in the past century using dated sediment cores from urban park lakes. Chemosphere 88, 1161–1169. http://dx.doi.org/10.1016/j.chemosphere.2012.03.061.

Li, H.B., Yu, S., Li, G.L., Deng, H., Luo, X.S., 2011. Contamination and source differentiation of Pb in park soils along an urban–rural gradient in Shanghai. Environ. Pollut. 159, 3536–3544. http://dx.doi.org/10.1016/j.envpol.2011.08.013.

Liu, Y.Q., 1995. Study and application of the soil environmental background values in Fujian coastal zone. Mar. Environ. Sci. 14, 68–73.

Michael, K., Vojtěch, E., Vladislav, C., Martin, 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.

Monna, F., Hamer, K., Lévêque, J., Sauer, M., 2000. Pb isotopes as a reliable marker of early mining and smelting in the Northern Harz province (Lower Saxony, Germany). J. Geochem. Explor. 68, 201–210. http://dx.doi.org/10.1016/s0375-6742(00)00005–4.

Müller, G., 1969. Index of geoaccumulation in sediments of the Rhine River. GeoJournal 2, 108–118.

Mulligan, C.N., Yong, R.N., Gibbs, B.F., 2001. An evaluation of technologies for the heavy metal remediation of dredged sediments. J. Hazard. Mater. 85, 145–163. http://dx.doi.org/10.1016/S0304-3894(01)00226–6.

N'Guessan, Y.M., Probst, J.L., Bur, T., Probst, A., 2009. Trace elements in stream bed sediments from agricultural catchments (Gascogne region, S-W France): where do they

come from? Sci. Total Environ. 407, 2939–2952. http://dx.doi.org/10.1016/j.scitotenv.2008.12.047.

Peng, B., Yan, X.Y., Yu, C.X., Tan, C.Y., Tu, X.L., Liu, Q., Yang, K.S., Xiao, M., Xu, J.Z., 2011. Heavy metal contamination of inlet sediments of the Xiangjiang River and Pb isotopic geochemical implication. Acta Geol. Sin. 85, 282–299.

Qiao, Y.M., Yang, Y., Gu, J.G., Zhao, J.G., 2013. Distribution and geochemical speciation of heavy metals in sediments from coastal area suffered rapid urbanization, a case study of Shantou Bay, China. Mar. Pollut. Bull. 68, 140–146. http://dx.doi.org/10.1016/j.marpolbul.2012.12.003.

Sun, G.X., Wang, X.J., Hu, Q.H., 2011. Using stable lead isotopes to trace heavy metal contamination sources in sediments of Xiangjiang and Lishui Rivers in China. Environ. Pollut. 159, 3406–3410. http://dx.doi.org/10.1016/j.envpol.2011.08.037.

Townsend, A.T., Seen, A.J., 2012. Historical lead isotope record of a sediment core from the Derwent River (Tasmania, Australia): a multiple source environment. Sci. Total Environ. 424, 153–161. http://dx.doi.org/10.1016/j.scitotenv.2012.02.011.

Yu, R.L., Hu, G.R., Wang, L.J., 2010. Speciation and ecological risk of heavy metals in intertidal sediments of Quanzhou Bay, China. Environ. Monit. Assess. 163, 241–252. http://dx.doi.org/10.1007/s10661-009-0830-z.

Yu, R.L., Yuan, X., Zhao, Y.H., Hu, G.R., Tu, X.L., 2008. Heavy metal pollution in intertidal sediments from Quanzhou Bay, China. J. Environ. Sci. china 20, 664–669. http://dx.doi.org/10.3321/j.issn:1001-0742.2008.06.005.