Contamination of heavy metals and isotopic tracing of Pb in intertidal surface sediments of Jinjiang River Estuary, SE China

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ABSTRACT

Contamination of 14 heavy metals and isotopic tracing of Pb were studied in the intertidal surface sediments of Jinjiang River Estuary, southeast China. Concentrations of the heavy metals in the sediments decrease as Fe > Ti > Mn > Zn > Cu > Cr > Pb > V > Ni > Sn > Co > Sb > Cd > Hg. Except Fe, Ti and V, the other elements show higher concentrations than their background values at most sampling sites. The assessment results of geo-accumulation index and potential ecological risk index indicate that the intertidal surface sediments are polluted by some heavy metals (Cd, Hg, Cu, Mn, Zn, Sb, Sn, Pb, Cr, Ni and Co) and show very high ecological risk with the main contributors of Cd and Hg. Results of multivariate statistic analysis suggest that Fe, V, Ti and Cr are mainly influenced by natural sources; Cu, Ni, Sn and Mn are mainly influenced by mining industries and the combustion of fossil fuel; Pb and Hg are mainly influenced by coal combustion and Pb-Zn ore; Zn, Cd, Co and Sb are mainly influenced by agricultural activities. The results of Pb isotope tracing show that total Pb in the sediments is mainly from parent material (44.0%—50.0%), Pb-Zn ore (35.8%—41.7%) and vehicle exhaust (7.8%—18.2%).

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1. Introduction

Heavy metal pollution in offshore ecological environments has drawn wide attention by researchers all over the world. Many researchers studied the distribution, speciation, ecological risk and source analysis of heavy metals (Fan et al., 2014; Qiao et al., 2013; Sheykhi and Moore, 2013; Shikazono et al., 2012; Yu et al., 2010; Zhao and Li, 2013). It was reported that more than 99% of heavy metal pollutants would deposit in sediments after being discharged into waterbodies (Sun et al., 2010). There are several assessment methods such as geo-accumulation index and potential ecological risk index to evaluate heavy metal pollution in sediment, but each method has its own limitations (Ding et al., 2005). Multivariate statistical analysis method such as cluster analysis has been widely used in the source analysis of heavy metals (Anju and Banerjee, 2012). However, this method may result in some subjectivity in

the judgment and interpretation of some source apportionment results. Moreover, the multivariate statistical analysis method generally can not give the contribution rate of each specific source. It has been proved that Pb isotopic composition is a useful tracer for Pb pollution assessment and provenance determination, and many studies using sediments as the historical archive of Pb contamination (Fillion et al., 2014; Frostick et al., 2011). Lead isotope fingerprint can be used not only to identify Pb pollution sources, but also to quantitatively evaluate the contribution rates of various sources combined with a linear mixing model of Pb isotopic ratios (Cheng and Hu, 2010).

Jinjiang River is the third longest river in Fujian province, southeast China, with the total length of 182 km and the total catchment area of 5629 km^2. It is the biggest river in Quanzhou region with the mean annual runoff of 55.02×10^8 m^3 and the mean suspended sediment concentration of 0.46 kg m^{-3}. After flowing through many counties and cities, Jinjiang River eventually flows into Quanzhou Bay, which is the famous starting point of the Maritime Silk Road in ancient China. Thus, the pollution level of Jinjiang River can affect the water quality of Quanzhou Bay. Within the catchment area of Jinjiang River, there are hundreds of

industrial enterprises, including lead-zinc mining, metal smelting and processing, printing and dyeing, tanning and other diverse chemical industrials, as well as many sewage treatment plants and farms. These pollution sources have inevitably resulted in a lot of discharged pollutants including heavy metals. The tidal reach, named Jinjiang River Estuary in this paper, is about 20 km long from the river mouth upward to Jinji floodgate, which was built in 1967 in Fengzhou town in Nan'an city for the purpose of flood control and irrigation for the upstream areas. The characteristics of hydrodynamic conditions and sediment transportation in the estuary are complicated due to the joint impact of the tide and the river water, as well as numerous discharge outlets of runoff and sewage along the banks. The contamination status of heavy metals in this study area can reflect the pollution level of heavy metals in the whole river to a certain extent. The estuary sediment acts as the main sink for heavy metals discharged into the river. It was reported that Jinjiang River Estuary had been polluted by heavy metals during the past few decades due to the rapid development of urbanization and industrialization in Quanzhou region (Wang et al., 2010). However, few systematic studies about the source analysis of heavy metals in Jinjiang River Estuary have been carried out up to now. Therefore, the aims of this study are: 1) to investigate the concentration level of 14 heavy metals (Fe, Ti, Mn, Zn, Cu, Cr, Pb, V, Ni, Sn, Co, Sb, Cd and Hg) in the intertidal surface sediments of Jinjiang River Estuary; 2) to assess the contamination degree of heavy metals using the methods of geo-accumulation index and potential ecological risk index; 3) to discuss the natural or anthropogenic sources of heavy metals using multivariate statistical analysis; 4) to estimate the contribution rates of natural and anthropogenic Pb sources to the Pb accumulated in the sediments using Pb isotopic tracing technology, in order to provide scientific data for the effective environmental management.

2. Materials and methods

2.1. Sampling and preparation

Fourteen sampling sites were set from the river mouth to Jinji floodgate, named site 1 to site 14, in the intertidal zone of Jinjiang River Estuary (Fig. 1). In December 2012, surface sediment (0–5 cm) was collected at each sampling site using a Van Veen grab sampler during the ebb tide. The pH, salinity and redox potential (Eh) of the sediments were measured on the spot with an Orion pH828 meter, a DW-1 oxidation-reduction potentiometer and an Orion 115A multipurpose salinity meter, respectively. The sediment samples were sealed in polyethylene bags and transported to the laboratory, freeze dried prior to further analysis. About 1.0 g of each dry sediment sample was taken for the analysis of grain size distribution using a Winner 2000 laser particle granularity analyzer. The remaining sample was then ground using an agate pestle and mortar and sieved through a 63 μm nylon sieve. The section under the sieve (<63 μm) was kept in a sealed plastic vessel at 4 °C for further analysis.

In order to trace Pb accumulated in the sediments of Jinjiang River Estuary, parent material, vehicle exhaust, coal and Pb-Zn ore were chosen as potential sources. Parent material is the underlying geological material in which soil horizons form. The soils within the basin developed mainly from granite. The parent material samples were collected from the uncontaminated soils within the basin. The vehicle exhaust dust samples were collected from the exhaust pipes of some vehicles in some local parking lots. The coal dust samples were collected from some local coal-fired power plants and some coal-fired enterprises. The Pb-Zn ore samples were collected from the upstream Pb-Zn deposits. The sampling sites of these potential source materials are also illustrated in Fig. 1. All

these samples were systematically analyzed for Pb isotope compositions.

2.2. Analysis of sediment physicochemical parameters

Calcium carbonate ($CaCO_3$) content in the sediment was estimated by determining the amount of CO_2 released from the reaction of $CaCO_3$ with hydrochloric acid (Loring and Rantala, 1992). The organic matter content in the sediment was estimated by determining the loss-on-ignition (LOI) after heating samples at 550 °C for 6 h (Bindler et al., 2012; Tam and Wong, 2000). The content of S^{2-} was determined using the method described by Janaki-Raman et al. (2007).

2.3. Analysis of heavy metals

For the determination of heavy metal concentrations, 0.1 g of each dry sediment sample was digested by the mixture acid of HNO_3-HCl-H_2O_2-HF, and diluted to 100 mL with deionized water for further analysis (Yu et al., 2016). The concentration of Hg was determined using an automatic mercury analyzer (NIC RA-3, Japan), and the concentrations of the other 13 elements were determined using an inductively coupled plasma-mass spectrometer (ICP-MS, ELAN9000, Perkin-Elmer, USA). All the solutions were analyzed in triplicates. Background correction and matrix interference were monitored throughout the analyses. The detection limits for the examined metals are listed in Table 1. A sediment reference material, GBW07314, issued by the State Oceanographic Administration of China, was processed with the same digestion procedure. The analytical results of the examined metals for the reference material GBW07314 showed a good agreement with the reference values with the recovery range of 93%–110% (Table 2). The relative error was less than 10% and the relative standard deviation (RSD) was less than 5%.

2.4. Analysis of Pb isotope compositions

The analysis of Pb isotopic composition in the sediment samples and the potential source samples was conducted in the clean laboratory of Beijing Research Institute of Uranium Geology. For the determination of total isotopes, sediments were digested by mixture acid HNO_3-HF. For the determination of nitric-extractable isotopes, sediments were extracted with 0.5 mol L^{-1} HNO_3, and the extraction of residual isotopes is similar with the method for total isotopes. Pb in the total digestion solution, nitric-extractable solution and residual solution was separated and purified according to the analytical procedures of Chinese geological mineral industry standard DZ/T 0184.12–1997. The isotopic compositions of Pb were determined by thermal ionization mass spectrometry (VG354, VGInstruments, UK). The reference materials NBS981 (National Bureau of Standards, USA) was employed for the quality control in the analysis process of Pb isotopic ratios. The measured $^{208}Pb/^{206}Pb$, $^{207}Pb/^{206}Pb$ and $^{207}Pb/^{204}Pb$ of the reference material NBS981 were 2.1681 ± 0.0008, 0.91462 ± 0.00033 and 15.4910 ± 0.0097, respectively, with the relative standard deviations of less than 0.05%.

2.5. Quality assurance and data processing

Guaranteed reagents were used in the analysis of heavy metal concentrations, and metal-oxide-semiconductor (MOS) reagents with very little impurities were used in the analysis of Pb isotopic ratios. Double de-ionized water from a MILLI-Q system was used to prepare the solutions and dilutions. All the glassware and Teflon vessels were previously soaked with 20% (V/V) guaranteed HNO_3
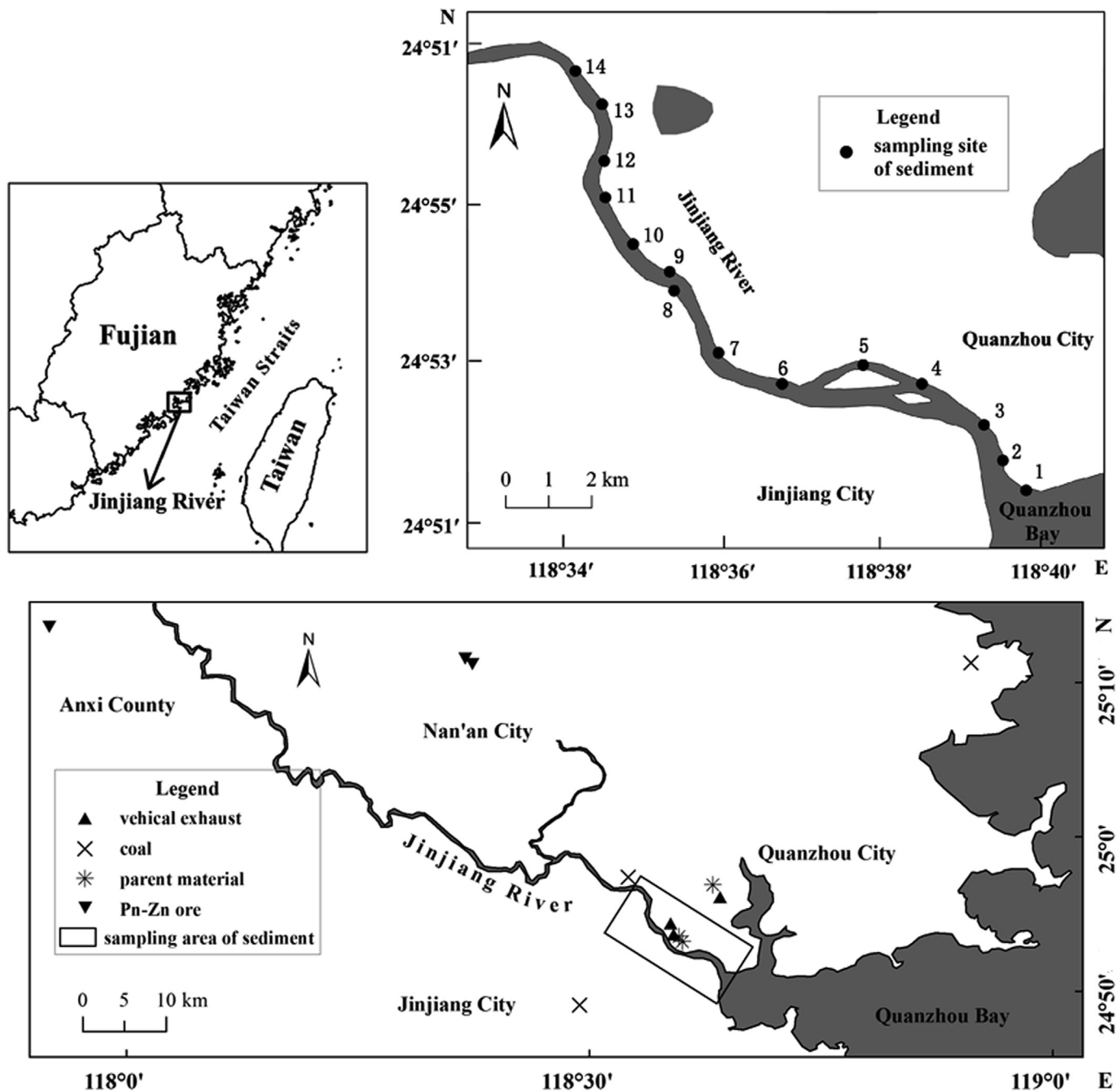
Fig. 1. Sampling map.

Table 1
Detection limits ($mg \cdot kg^{-1}$) for the examined metals in sediment samples.

Element	Fe	Ti	Mn	Zn	Cu	Cr	Pb	V	Ni	Sn	Co	Sb	Cd	Hg
Detection limits	0.05	0.009	0.01	0.02	0.01	0.05	0.001	0.098	0.01	0.02	0.01	0.001	0.002	0.009

solution overnight and then rinsed thoroughly with de-ionized water, and blow-dried prior to usage. Normal precautions for the analyses were observed throughout. Equipment condition and quality control were assured by measuring a standard solution after every 10 samples in the analysis of heavy metal concentrations, and every 5 samples in the analysis of Pb isotopic ratios. The data were analyzed by Microsoft Excel and SPSS software in this study.

3. Results and discussion

3.1. Physicochemical parameters of the sediments

The main physicochemical parameters of the surface sediments are listed in Table 3. From site 1 to site 14, the pH values of the sediments decrease from 8.0 to 6.8, and the salinity values decrease

Table 2
Analytical results of the examined metals for the reference material GBW07314.

Element	Fe	Ti	Mn	Zn	Cu	Cr	Pb	V	Ni	Co	Sb	Cd	Hg
Reference value (mg·kg^{-1})	37,500	4942	744	87	31	86	25	103	34.3	14.2	1.40	0.20	0.048
Measured value (mg·kg^{-1})	38,888	4690	780	90.9	30.1	94	23.3	109	32.3	14.9	1.53	0.22	0.052
Recovery (%)	104	94.9	105	104	97.1	109	93.2	106	94.2	105	109	110	108
Relative error (%)	3.7	5.1	4.8	4.5	3.2	9.7	7.0	5.8	5.7	4.9	8.9	7.9	7.8
Relative standard deviation (%)	2.9	4.9	4.2	4.8	2.7	5.0	3.9	3.8	3.3	3.7	3.6	4.8	4.1

Table 3
Physic-chemical parameters of the intertidal surface sediments in Jinjiang River Estuary.

Site	pH	Salinity (‰)	Eh (mV)	CaCO$_3$ (%)	LOI (%)	S^{2-} (%)	Dav (μm)	Clay (%)	Silt (%)
1	8.0	8.4	−98	2.4	11.5	0.18	7.4	25.9	65.1
2	7.8	3.3	−85	2.0	10.0	0.67	7.4	25.7	69.8
3	7.9	3.2	133	1.9	13.1	0.31	12.0	20.9	58.8
4	7.8	1.5	−42	1.8	10.4	0.50	5.8	27.3	68.6
5	7.8	1.1	−144	1.7	10.1	0.48	12.0	20.7	60.0
6	7.5	1.2	−105	0.2	10.4	0.31	6.0	25.4	71.0
7	7.5	1.4	−71	1.6	9.7	0.38	6.2	25.7	70.5
8	7.5	0.4	−56	3.2	8.6	0.44	6.6	25.2	70.8
9	7.4	0.8	−3.0	0.3	10.7	0.34	5.9	26.0	70.0
10	7.1	0.5	65	6.2	9.9	0.20	8.9	22.5	64.4
11	7.2	0.4	96	3.4	10.7	0.31	6.4	27.2	63.6
12	7.2	0.2	9.0	4.5	10.0	0.27	7.9	23.3	63.0
13	6.9	0.1	122	1.7	10.1	0.57	10.6	20.4	61.7
14	6.8	0.1	124	0.4	10.2	0.20	14.3	17.9	55.5
Mean	7.5	1.9	−4.1	2.4	10.4	0.38	8.6	23.7	64.8

from 8.4‰ to 0.1‰, reflecting the decreasing influence of sea water upstream. The oxidation reduction potential (Eh) values of the sediments range from −144 mV to 133 mV, indicating a reductive environment. The CaCO$_3$ contents range from 0.2% to 6.2% with the maximum at site 10 due to the nearby oyster farming. LOI values of the sediments show a range of 8.6%–13.1% with the maximum at site 3, where there are a lot of *Spartina alterniflora* loisel. The S^{2-} contents range from 0.18% to 0.67%, implying a reductive environment with considerable sulfides. The median grain sizes of the sediments range from 5.8 μm to 14.3 μm, with the mean of 8.6 μm. The abundant weeds growing in the intertidal zone sediments may affect the size of sediment particle (Davies and Gibling, 2010). The range of clay (grain size 0−2 μm) content is 17.9%−27.3% with the mean of 23.9% and the range of silt (grain size 2−20 μm) content is 55.5%−71.0% with the mean of 64.8%, indicating a clay silt deposition environment.

3.2. Level of heavy metals

The concentrations of the investigated heavy metals in the surface sediments are demonstrated in Fig. 2. The mean concentrations (mg·kg^{-1}) show the order of Fe (40749) > Ti (2168) > Mn (1264) > Zn (331) > Cu (102) > Cr (99.9) > Pb (95.6) > V (67.8) > Ni (28.5) > Sn (15.5) > Co (13.1) > Sb (1.93) > Cd (1.59) > Hg (0.486). Fe, Ni, V, and Ti present the highest concentrations at site 1, which is located at the junction of Jinjiang River and Quanzhou Bay. Most metals in the river water are more likely to deposit into sediment at the river-sea junction due to the strong tidal action in the interchange and the frequent material exchange between overlying water and sediment. Concentrations of the other heavy metals present no consistent pattern because there are thousands of runoff and sewage discharge outlets along the banks, and each discharge may contain different heavy metals. The changing concentrations of heavy metals are closely related to various human activities.

The surface sediments in Jinjiang River Estuary mainly derive from the soils within the basin due to the frequent surface runoff.

The elemental geochemical background values in the reference of Chen et al. (1992) were determined from 123 soil samples, which were collected all over Fujian province and contained main soil types and parent materials. Thus the geochemical background values of heavy metals in Fujian province soil (Chen et al., 1992) can be adopted as the background values of heavy metals in Jinjiang River Estuary (illustrated in Fig. 2). The concentrations of Ti, Fe and V at most sampling sites are lower than their background values, suggesting no enrichment in the study area. On the contrary, the concentrations of Cr, Mn, Co, Ni, Cu, Zn, Cd, Pb, Sb, Hg and Sn at most sampling sites are higher than their background values, indicating obvious impact of human activities.

The comparison of heavy metal concentrations in this study and in the sediments of other domestic (especially in Fujian province) and overseas estuaries or bays is listed in Table 4. The concentrations of Zn, Cu, Cr, Sb, Cd and Hg in this study are obviously higher than other areas. The concentrations of Pb are comparable with those in Jiulong River, but higher than those in the other areas. The concentrations of Fe are comparable with those in Jiulong River and Kachemrk Bay, but higher than those in the other areas. The concentration of Mn is similar with those in Quanzhou Bay and Jiulong River, while higher than other areas. The concentration of Co is comparable with those in Quanzhou Bay and Jiulong River, while lower than that in West Xiamen Bay. The concentration of Ni is lower than that in Kachemrk Bay, while comparable with other areas.

3.3. Pollution assessment of heavy metals

3.3.1. Geo-accumulation index

Geo-accumulation index (I_{geo}), first proposed by Müller (1969), was employed to evaluate the pollution degree of heavy metals in the sediments.
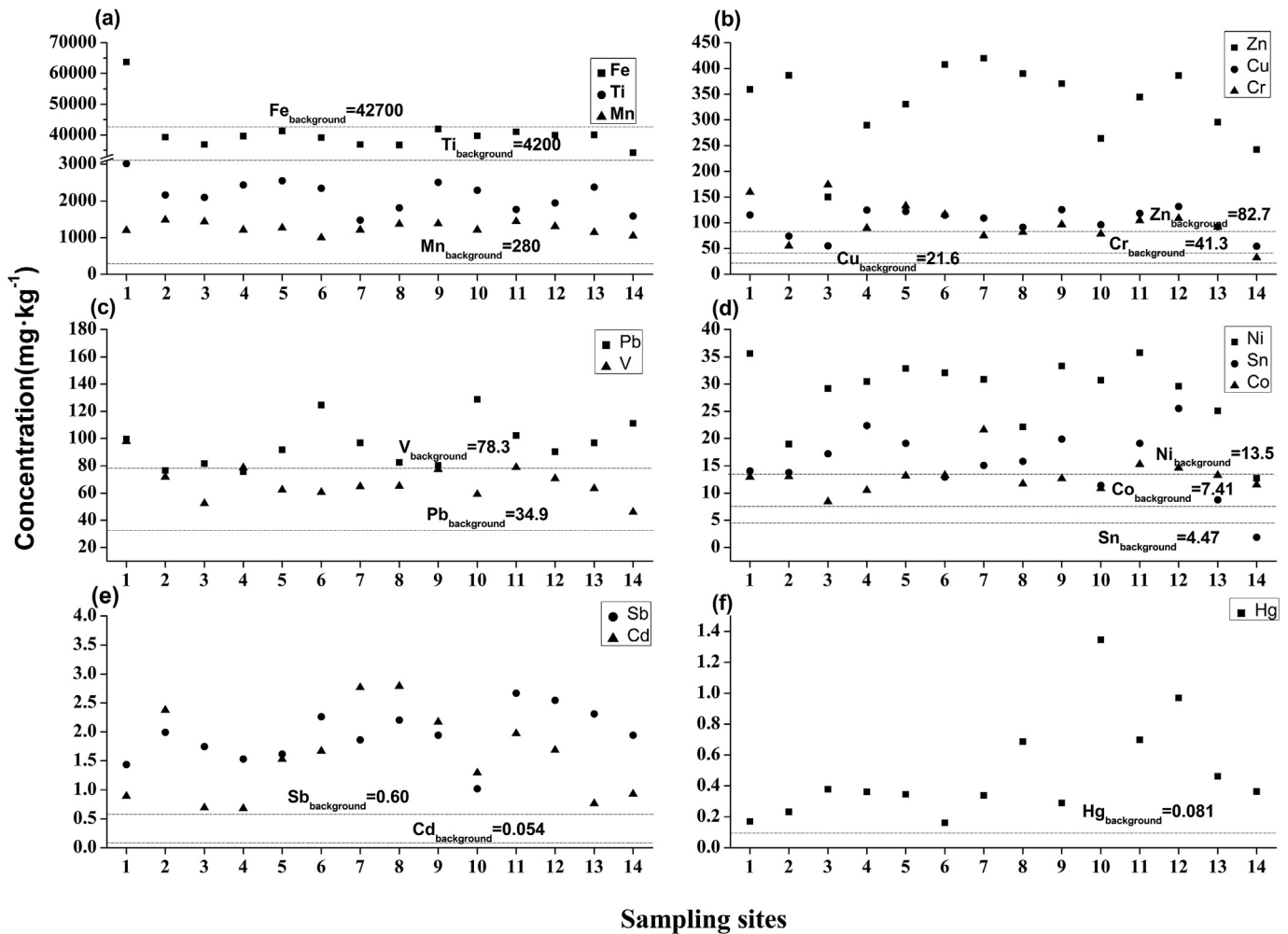
Fig. 2. Concentrations of heavy metals in the intertidal surface sediments of Jinjiang River Estuary: (a)Fe, Ti and Mn; (b)Zn, Cu and Cr; (c)Pb and V; (d)Ni, Sn and Co; (e) Sb and Cd; (f)Hg. Background values are element background values of Fujian soil (Chen et al., 1992).

Table 4
Comparison of heavy metal concentrations (mg·kg^{-1}) in surface sediments of Jinjiang River Estuary and other areas.

Study area	Fe	Ti	Mn	Zn	Cu	Cr	Pb	Reference
Jinjiang River Estuary	40749	2168	1264	331	102	99.9	95.6	This study
Quanzhou Bay	38,455	3431	1295	187	60.8	84.7	67.0	Yu et al., 2016
Jiulong River	40,971	–	1133	172	83.0	93.6	103	Lin et al., 2016
West Xiamen Bay	32,783	3847	674	258	52.5	74.9	37.5	Yang et al., 2016
North Minjiang River Estuary	–	–	–	104	26.3	65.5	39.1	Li et al., 2015
Kachemrk Bay, USA	40,800	–	649	95.1	35.6	76.7	11	Apeti and Hartwell, 2015
Mahshahr Bay, Persian Gulf	–	–	488	183.4	26.5	70	–	Vaezi et al., 2015

Study area	V	Ni	Sn	Co	Sb	Cd	Hg	Reference
Jinjiang River Estuary	67.8	28.5	15.5	13.1	1.93	1.59	0.486	This study
Quanzhou Bay	83.8	26.8	12.6	11.9	0.89	0.64	0.107	Yu et al., 2016
Jiulong River	71.0	28.2	–	14.9	1.06	0.96	0.166	Lin et al., 2016
West Xiamen Bay	69.0	23.9	–	19.9	–	–	–	Yang et al., 2016
North Minjiang River Estuary	80.2	30.5	–	–	0.6	–	0.05	Li et al., 2015
Kachemrk Bay, USA	–	38.9	–	–	–	–	0.09	Apeti and Hartwell, 2015
Mahshahr Bay, Persian Gulf	–	29.7	–	–	–	–	–	Vaezi et al., 2015

— denotes data are not available.

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

Where, C_n is the measured concentration of the examined metal n in the sediment. B_n is the geochemical background value of metal n in Fujian province soil (Chen et al., 1992). The factor k, generally

taken 1.5, is used to correct the possible variations of the background data due to lithogenic effects. The correspondence between the pollution degree of heavy metals and the I_{geo} values is as follows: non-pollution ($I_{geo} < 0$), slight pollution ($0 \leq I_{geo} < 1$), moderate pollution ($1 \leq I_{geo} < 2$), moderate to strong pollution ($2 \leq I_{geo} < 3$), strong pollution ($3 \leq I_{geo} < 4$), strong to extreme pollution ($4 \leq I_{geo} < 5$) and extreme pollution ($I_{geo} \geq 5$).

The calculated I_{geo} values of the 14 heavy metals in this study are shown in Fig. 3. Fe, V and Ti show non-pollution ($I_{geo} < 0$) at all sampling sites. Pb, Cr, Ni and Co show slight pollution ($0 < I_{geo} < 1$) at most sampling sites. Cu, Mn, Zn, Sb and Sn show moderate pollution ($1 < I_{geo} < 2$) at most sampling sites. Hg shows moderate pollution ($0.77 \leq I_{geo} \leq 1.95$) at sites 3, 4, 5, 7, 9, 13 and 14, while moderate to strong pollution ($2.00 \leq I_{geo} \leq 3.83$) at sites 8, 10, 11 and 12. It is worth noting that the pollution degree of Cd is strong to extreme ($3.07 \leq I_{geo} \leq 5.10$) at all sampling sites, this may be associated with the human activities including upstream mining and metal smelting.

3.3.2. Potential ecological risk index

Potential ecological risk index (RI), first proposed by Hakanson (1980), is a relatively simple method to assess pollution level and potential ecological risk of contaminants including heavy metals in sediment. The calculation formulae of potential ecological risk index are as follows:

$$C_f^i = C_i \big/ C_n^i \tag{2}$$

$$E_r^i = T_r^i \times C_f^i \tag{3}$$

$$RI = \sum E_r^i \tag{4}$$

Where, C_f^i is the pollution factor of single element i; C_i is the measured concentration of element i in sediment; C_n^i is the background value of element i (Chen et al., 1992); E_r^i is the potential ecological risk index of element i; T_r^i is the biological toxic factor of element i, taken as Ti = Zn = Mn = 1, V = Cr = 2, Cu = Ni = Pb = Co = 5, Cd = 30, Hg = 40 (Hakanson, 1980; N'Guessan et al., 2009; Saleem et al., 2013). RI is the comprehensive potential ecological risk index of all the examined pollutants. Since the number of pollutants examined in this study is different from that in the
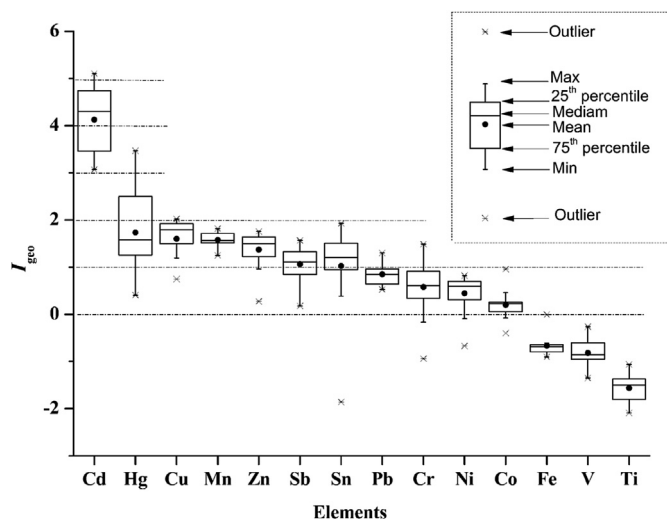
original reference (Hakanson, 1980), necessary adjustment of RI standard is made as shown in Table 5.

The calculated E_r^i and RI of the selected heavy metals are shown in Fig. 4. Cd shows an average E_r^i of 882 ($378 < E_r^i < 1550$), indicating it presents very high potential ecological risk in the study area, especially at the sites of 2, 7, 8, 9, 11. Hg shows an average E_r^i of 240 ($80 < E_r^i < 665$), demonstrating considerable ecological risk. The E_r^i values of the other heavy metals are less than 40 ($0.35 < E_r^i < 30.5$), indicating their potential ecological risk almost can be ignored compared with Cd and Hg. However, considering the comprehensive potential ecological risk index (RI), the intertidal surface sediments of Jinjiang River Estuary show very high ecological risk ($628 < RI < 1954$) by heavy metals with the dominant contributors of Cd and Hg.

The evaluation results from the geo-accumulation index and potential ecological risk index are basically consistent, but there are some differences. For example, the geo-accumulation index shows that Mn presents moderate pollution, but potential ecological risk index shows that Mn presents low ecological risk. The reason is that the focuses of the two assessment methods are different. The geo-accumulation index can show the enrichment level of heavy metals but does not consider the biological danger of heavy metals, while the potential ecological risk index can make up for this deficiency by introducing the toxicity of heavy metals. Therefore, combining these two evaluation methods can make the assessment results of the heavy metal pollution more comprehensive and rational.

3.4. Multivariate statistical analysis

Pearson's correlation coefficients among the heavy metals and with the physic-chemical parameters in the surface sediments are shown in Table 6. There are significant positive correlations among the metals in the groups of Fe-Ti-V, Ni-Cu-Sn and Zn-Cd-Co, illustrating the possible similar geochemical behaviors such as source and migration for the metals within each group. In addition, Ni shows significant positive correlation with Cr and V, implying the possible similar geochemical behaviors between Ni and these two elements. The pairs of V-Cu and Ti-Cr show significant positive correlations, implying the possible similar behaviors for each pair. Mn shows significant negative correlation with Pb, while Mn, Pb, Sb and Hg show no significant correlation with the other metals, suggesting their different geochemical behaviors with the other metals. Many industrial and mining enterprises as well as numerous domestic sewage discharge outlets located around Jingjiang River Estuary have significant contribution to the sources of above heavy metals.

Cr, Fe, Ti, V, Sn, Ni and Mn show obviously positive correlation with pH, indicating that pH plays an important role in the sedimentation of above metals. Generally, most of the heavy metal pollutants would deposit in sediments after being discharged into waterbodies, but the heavy metals in sediments would release when pH declines. Fe, V and Ti show significant positive correlation with salinity. Most of the heavy metals, especially Zn, Cu and Cd, show negative correlation with Eh, implying that most of the metals do not mainly exist in the reducible fractions since the study

Fig. 3. Box plots of geo-accumulation index of the heavy metals in the sediments.

Table 5
Grade standards for E_r^i and RI.

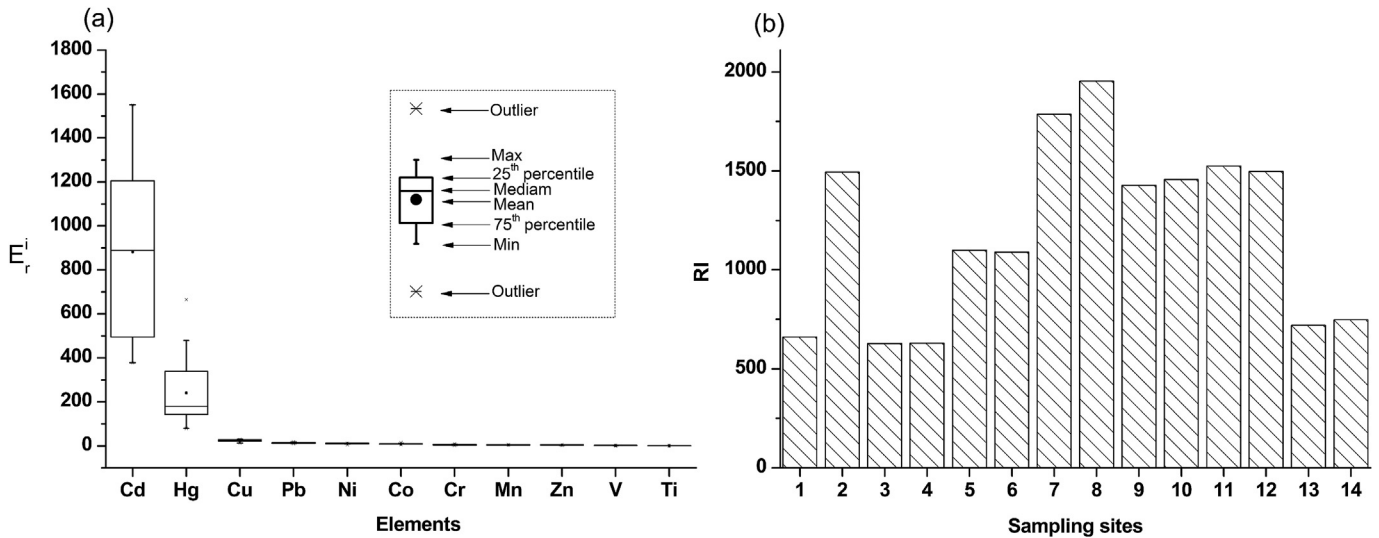| E_r^i	RI	Grades of potential ecological risk
<40	<110	low
40–80	110–220	moderate
80–160	220–440	considerable
160–320		high
≧320	≧440	very high

Fig. 4. The potential ecological risk indices of heavy metals. (a) E_r^i value of each metal in the studied area. (b) RI value of the studied metals for each site.

Table 6
Pearson's correlation coefficients among the heavy metals and physic-chemical parameters in the sediments.

	Fe	Ti	Mn	Zn	Cu	Cr	Pb	V	Ni	Sn	Co	Sb	Cd	Hg
Fe	1	0.725[b]	−0.036	0.190	0.365	0521	0.031	0.798[b]	0.495	0.107	0.005	−0.285	−0.241	−0.225
Ti		1	−0.096	−0.028	0.355	0.541[a]	−0.049	0.537[a]	0.462	0.164	−0.393	−0.446	−0.448	−0.253
Mn			1	−0.003	−0.043	0.167	−0.655[a]	0.263	0.111	0.530	−0.078	0.161	0.388	0.141
Zn				1	0.602[a]	−0.204	−0.030	0.458	0.200	0.267	0.681[b]	0.374	0.745[b]	−0.149
Cu					1	0.236	−0.023	0.625[a]	0.743[b]	0.679[b]	0.395	0.114	0.200	0.081
Cr						1	−0.111	0.304	0.683[b]	0.440	−0.221	−0.116	−0.347	−0.173
Pb							1	−0.297	0.087	−0.527	0.098	−0.140	−0.163	0.335
V								1	0.556[a]	0.473	0.185	−0.017	0.078	−0.178
Ni									1	0.614[a]	0.215	−0.118	−0.022	0.052
Sn										1	0.091	0.159	0.209	0.131
Co											1	0.323	0.588[a]	−0.092
Sb												1	0.344	−0.067
Cd													1	0.044
Hg														1
pH	0.434	0.471	0.352	0.086	0.141	0.591[a]	−0.489	0.439	0.374	0.457	−0.129	−0.360	0.029	−0.481
Sal.	0.831[b]	0.570[a]	0.094	0.008	−0.034	0.529	−0.145	0.591[a]	0.258	0.008	−0.096	−0.399	−0.231	−0.444
Eh	−0.342	−0.358	0.054	−0.695[b]	−0.502	−0.123	0.155	−0.410	−0.270	−0.320	−0.304	0.182	−0.424	0.384
CaCO₃	0.079	−0.068	0.292	−0.065	0.132	0.026	0.211	0.110	0.184	0.245	−0.060	−0.172	0.043	0.901[b]
LOI	0.012	0.188	0.222	−0.671[a]	−0.297	0.655[a]	−0.131	−0.191	0.254	0.126	−0.395	−0.093	−0.543	−0.240
S²⁻	−0.281	0.036	0.314	0.202	−0.040	−0.234	−0.587[a]	0.019	−0.255	0.127	0.063	0.185	0.235	−0.306
Dav	−0.219	−0.100	−0.205	−0.704[b]	−0.631[a]	0.007	0.154	−0.645[a]	−0.479	−0.516	−0.373	−0.173	−0.532	0.019
Clay	0.310	0.140	0.326	0.613[a]	0.576[a]	0.070	−0.255	0.736[b]	0.502	0.545[a]	0.312	0.117	0.469	−0.128

[a] Correlation is significant at the 0.05 level (2-tailed).
[b] Correlation is significant at the 0.01 level (2-tailed).

area is in a reducing environment. Except Hg, the other metals show no correlation with CaCO₃, indicating that most of the metals do not mainly exist in the form of carbonate in the sediments. All the metals show no significant positive correlation with S²⁻, indicating that the metals are not mainly in the form of sulfide in the sediments, either. Except Cr, the other metals show no significant correlation with LOI, suggesting that the content of organic matter barely affects the deposition of most metals in the sediments. Most of the heavy metals, especially V, Zn, Cu, Sn, Ni and Cd show positive correlation with the clay content, while negative correlation with the median grain size of the sediments, indicating that most metals exist in the fine sediment particles.

Hierarchical cluster analysis was performed on the Z-Scores normalized data by means of ward's method, using the squared Euclidean distance as the similarity measure. The metals are grouped into 4 clusters (Fig. 5), basically consistent with the results of correlation analysis. Cluster 1 consists of Fe, V, Ti and Cr,

illustrating that these four elements may derive from similar source. According to above discussion, the concentrations of Ti, Fe and V are lower than their background values at most sampling sites, and these three heavy metals show non-pollution. This result indicates that the metals in cluster 1 are mainly influenced by natural sources. Cluster 2 consists of Cu, Ni, Sn and Mn, illustrating that Cu, Ni, Sn and Mn may derive from similar sources. It is reported that Mn is the main rock-forming mineral element (Yuan et al., 2004). Mn is one of the major constituent in rocks mined in Fujian province (Zhang, 2012). Ni is associated to the combustion of fossil fuel (Lu et al., 1995). It was reported that Mn and Ni in the surface sediments of Jiulong River (the second largest river in Fujian province, situated in about 90 km to the southeast of Jinjiang River) were mainly influenced by mining industries and the combustion of fossil fuel, respectively (Wang et al., 2014). Jiulong River shares some upstream sources with Jinjiang River, and the geological composition and economic pattern (including mining and smelting
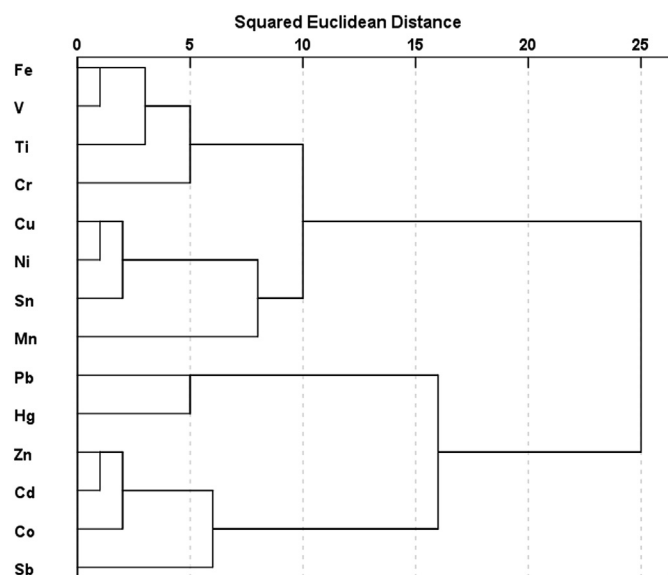
Fig. 5. Cluster result of heavy metals in the sediments.

Fig. 6. Plot of $^{206}Pb/^{207}Pb$ vs $^{206}Pb/^{208}Pb$ in the sediments and the potential source materials.

industries) of the two basins are similar. Thus the sources of Mn and Ni in the surface sediments of Jinjiang River Estuary might be similar to those in Jiulong River. The result of multivariate statistical analysis suggests that Cu, Ni, Sn and Mn may derive from the similar sources. Cu and Sn may have other sources, but the major sources may be mining industries and the combustion of fossil fuel. Cluster 3 consists of Pb and Hg which may derive from similar source. It is reported that Pb accumulated in surface sediments may derived from coal combustion and Pb-Zn deposited (Lin et al., 2016), and Hg may derive from coal combustion (Liu et al., 1998). This result indicates that the metals in cluster 3 are mainly influenced by coal combustion and Pb-Zn ore. Cluster 4 consists of Zn, Cd, Co and Sb which may derive from similar source. It is reported that Cd, Zn and Pb are commonly found in chemical fertilizers and pesticides (Gray et al., 1999), and Cd can generally be used as a marker for agricultural activities such as pesticides and fertilizers (Lv et al., 2015). This result indicates that the metals in cluster 4 are mainly influenced by agricultural activities.

3.5. Pb isotopic tracing in the sediments

Variations of Pb isotopic ratios generally reflect a mixture of several Pb sources with different isotopic signatures (Sun et al., 2011). Many studies on the characteristics of Pb isotopic ratios for the pollution source analysis have been reported (Townsend and Seen, 2012; Xu et al., 2014).

The plot of $^{206}Pb/^{207}Pb$ vs $^{206}Pb/^{208}Pb$ in the surface sediments and the potential sources of Jinjiang River Estuary are illustrated in Fig. 6. The ranges of $^{206}Pb/^{207}Pb$ and $^{206}Pb/^{208}Pb$ in the studied sediments are 1.1850—1.1889 and 0.4779—0.4798, respectively, and there is a good linear relationship between the two isotopic ratios ($R = 0.845$, $n = 14$). The Pb isotopic ratios in the residue fraction of sediments are near those of the parent material, while the Pb isotopic ratios in the nitric extraction of sediments are closer to those of the potential pollution sources, indicating that the Pb accumulated in the surface sediments may derived from natural processes of weathering, transport of bedrock, as well as from a range of anthropogenic activities. It is worth noting that the Pb isotopic ratios of coal are relatively farther from those of surface sediments than Pb-Zn ore and vehicle exhaust, suggesting that the coal combustion is not 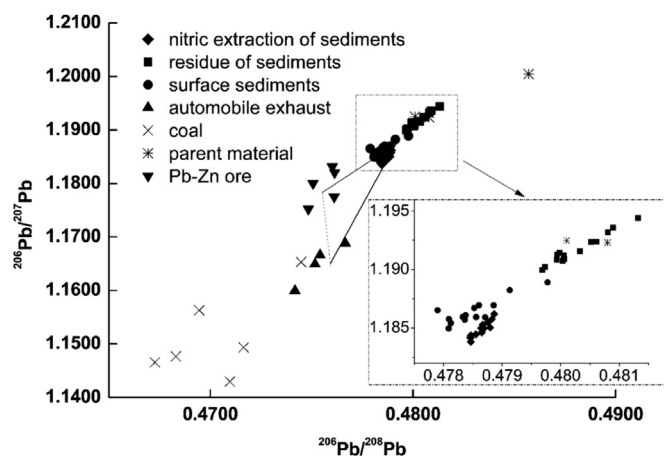the main Pb anthropogenic sources in the study area. There are good linear relationships among the Pb isotopic ratios of surface sediments, parent material and Pb-Zn ore ($R = 0.9584$), as well as among the Pb isotopic ratios of surface sediments, parent material and vehicle exhaust ($R = 0.8863$). Thus, a three-end-member model (Cheng and Hu, 2010) can be employed to calculate the contribution rates of parent material (f_1), Pb-Zn ore (f_2) and vehicle exhaust (f_3) to total Pb in the surface sediments:

$$f_1 + f_2 + f_3 = 1 \tag{5}$$

$$f_1 \times R_1 + f_2 \times R_2 + f_3 \times R_3 = R_S \tag{6}$$

$$f_1 \times N_1 + f_2 \times N_2 + f_3 \times N_3 = N_S \tag{7}$$

Where, R_1, R_2 and R_3 are $^{206}Pb/^{207}Pb$ ratios of parent material (1.195), Pb-Zn ore (1.180) and vehicle exhaust (1.165). N_1, N_2 and N_3 are $^{208}Pb/^{206}Pb$ ratios of parent material (2.074), Pb-Zn ore (2.102) and vehicle exhaust (2.104). R_S and N_S are the $^{206}Pb/^{207}Pb$ ratio and the $^{208}Pb/^{206}Pb$ ratio of each sediment sample. As shown in Table 7, the contribution rates of natural sources (parent material), Pb-Zn ore and vehicle exhaust to total Pb in the surface sediments are 44.0%—50.0%, 35.8%—41.7% and 7.8%—18.2%, respectively, indicating that Pb-Zn ore is the main anthropogenic source of Pb pollution in Jinjiang River Estuary.

4. Conclusions

Concentrations of 14 heavy metals in the intertidal surface sediments of Jinjiang River Estuary show the order of Fe > Ti > Mn > Zn > Cu > Cr > Pb > V > Ni > Sn > Co > Sb > Cd > Hg. The mean concentrations of Cr, Mn, Co, Ni, Cu, Zn, Cd, Pb, Sb, Sn and Hg are higher than their background values. The assessment results of geo-accumulation index and potential ecological risk index demonstrate that Jinjiang River Estuary has been polluted by some heavy metals (Cd, Hg, Cu, Mn, Zn, Sb, Sn, Pb, Cr, Ni and Co) and show very high ecological risk with the main contributors of Cd and Hg. Results of multivariate statistic analysis suggest that Fe, V, Ti and Cr mainly derive from natural sources; Cu, Ni, Sn and Mn are mainly influenced by mining industries and the combustion of fossil fuel; Pb and Hg are mainly influenced by coal combustion and Pb-Zn ore; Zn, Cd, Co and Sb are mainly influenced by agricultural activities.

Pb-Zn ore and vehicle exhaust are the two major anthropogenic sources of Pb in Jinjiang River Estuary based on the results of Pb isotopic tracing. The contribution rates of parent material, Pb-Zn

Table 7
Contributions of anthropogenic (Pb–Zn ore and vehicle exhaust) and natural Pb sources to total Pb in the sediments.

Site	Natural sources (%) Parent material	Anthropogenic sources (%)		Site	Natural sources (%) Parent material	Anthropogenic sources (%)	
		Pb–Zn ore	Vehicle exhaust			Pb–Zn ore	Vehicle exhaust
1	48.5	40.4	11.1	9	47.6	38.6	13.8
2	44.0	40.6	15.4	10	49.2	35.8	15.0
3	49.5	40.2	10.3	11	46.8	40.5	12.7
4	44.2	41.5	14.3	12	47.1	39.9	13.0
5	47.1	37.3	15.6	13	47.1	41.7	11.2
6	44.2	40.1	15.7	14	50.0	42.2	7.8
7	44.3	37.5	18.2	Mean	46.8	39.7	13.5
8	45.5	39.4	15.1				

ore and vehicle exhaust to total Pb in the sediments are 44.0%–50.0%, 35.8%–41.7% and 7.8%–18.2%, respectively, according to the calculation results using a three-end-member model.

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