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Distribution, fractionation, and contamination assessment of heavy metals in offshore surface sediments from western Xiamen Bay, China

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Abstract Surface sediment samples were collected at 21 offshore sites in western Xiamen Bay, Southeast China. Total concentrations of Li, V, Cr, Co, Ni, Cu, Zn, Sr, Mn, Pb, Ba, Fe, and Ti were determined by inductively coupled plasma-optical emission spectrometry; Hg was determined by atomic fluorescence spectrometry. A modified BCR sequential extraction procedure was used to extract fractions of the above elements. Concentrations of Pb, Cr, and Hg at most sites met the primary standard criteria of Marine Sediment Quality except site S12 for Pb and S7 for Cr, while concentrations of Zn at 17 sites and Cu at seven sites exceeded the criteria. The mean concentration of Hg was three times higher than the background, with a possible source being the Jiulong River. Fe, Ti, Ba, Co, V, and Li dominated the residual phase, mainly from terrestrial input. Ni, Cr, Pb, and Hg in the non-residual phase varied largely between sites. Sr, Mn, Cu, and Zn were mainly in the non-residual fraction. Most sites showed considerable ecological risk; exceptions were site S7 (very high) and sites S10, S11, and S14 (moderate). Cu showed moderate-to-high pollution and Pb exhibited no-to-low pollution, while other metals had a non-pollution status according to their ratios of secondary phase to primary phase (RSP). Results of two assessment methods showed moderate pollution and a very high ecological risk for Cu, Zn, Ni, and Cr at site S7, which might be due to the local sewage treatment plant.

1 Introduction

In coastal areas, heavy metals, as persistent pollutants, are adsorbed or accumulated by deposits or suspended solids, or enriched in vivo, and are a potential threat to ecosystems. Heavy metals in the aqueous phase change with the hydrodynamic conditions, with high randomness. Compared to the aqueous phase, heavy metal concentrations in sediments are often many times higher, and their distribution is significantly regular. Both in China and abroad, many scholars have done assessments of heavy metal pollution (Zhu et al. 2011; Hu et al. 2011; Kumar et al. 2013; Lin et al. 2013; Ma et al. 2013). With increasing coastal urbanization and industrialization, various activities have resulted in frequent worsening of offshore environmental pollution in coastal areas in Xiamen.

While determining the total amount of heavy metals provides the status of contaminated sediments, further analyses are required to characterize the properties of migration, transformation, and bioavailability of heavy metals in the sediments. The presence of heavy metals in different forms is an important indicator by which to judge the response and toxicity of heavy metals and their ecological risk in sediments. Different forms of heavy metals have different activity, toxicity, and migration characteristics (Qin et al. 2012). Studying fractionation of heavy metals in sediments provides information on bioavailability and toxicity (Davutluoglu et al. 2010). In this study, we

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used a modified BCR sequential extraction procedure to extract different fractions of 14 elements (Li, V, Cr, Co, Ni, Cu, Zn, Sr, Mn, Pb, Ba, Fe, Ti, and Hg) in the surface sediments collected from western Xiamen Bay.

We performed analyses on offshore surface sediments from western Xiamen Bay with two main goals: (a) assess the pollution and potential ecologic risk degree by measuring total concentrations of heavy metals, and (b) evaluate the relative mobility and bioavailability of heavy metals by fractionation analysis.

2 Sampling and methods

2.1 Sampling

The studied area is located in western Xiamen Bay (24°27′16″N, 118°1′54″E), close to the Jiulong River estuary. Surface sediment samples (0–5 cm depth) were collected when the tide ebbed during January to July, 2013 at 21 sampling sites (Fig. 1). The sediment samples were sealed in plastic bags and frozen at −20 °C until analysis. After the samples were defrosted and air-dried at room temperature, small stones and conch debris in the sediments were removed. The sediment samples were then ground to powder using an agate mortar and pestle, and

filtered using a 63-μm nylon sieve. The sediments that passed through the sieve were collected in pre-cleaned polyethylene bags in preparation for analysis of physico-chemical parameters and elemental composition.

2.2 Measurement of physico-chemical parameters

We measured several physico-chemical parameters of the sediments in the laboratory, including pH, loss-on-ignition (LOI), and total carbon (TC). The pH was determined using a pH meter (Model 828, USA). TC was tested using a TOC analyzer (Multi N/C2100, Germany). Organic matter content of the sediments was estimated by LOI which was determined after heating samples at 550 °C for 5 h (Tam and Wong 2000; Bindler et al. 2012).

2.3 Analysis of total heavy metals

Each sediment sample (0.2000 g) was placed in a Teflon vessel and digested with 6 mL HNO_3, 2 mL HCl, and 2 mL HF in a microwave digestion instrument (Multiwave3000, Anton Paar GmbH) and diluted to 50 mL with 3 % HNO_3. Quality was controlled by preparing a reagent blank and a marine sediment reference material (GBW 07314, China). Total concentrations of Li, V, Cr, Co, Ni, Cu, Zn, Sr, Mn, Pb, Ba, Fe, and Ti were determined by inductively coupled
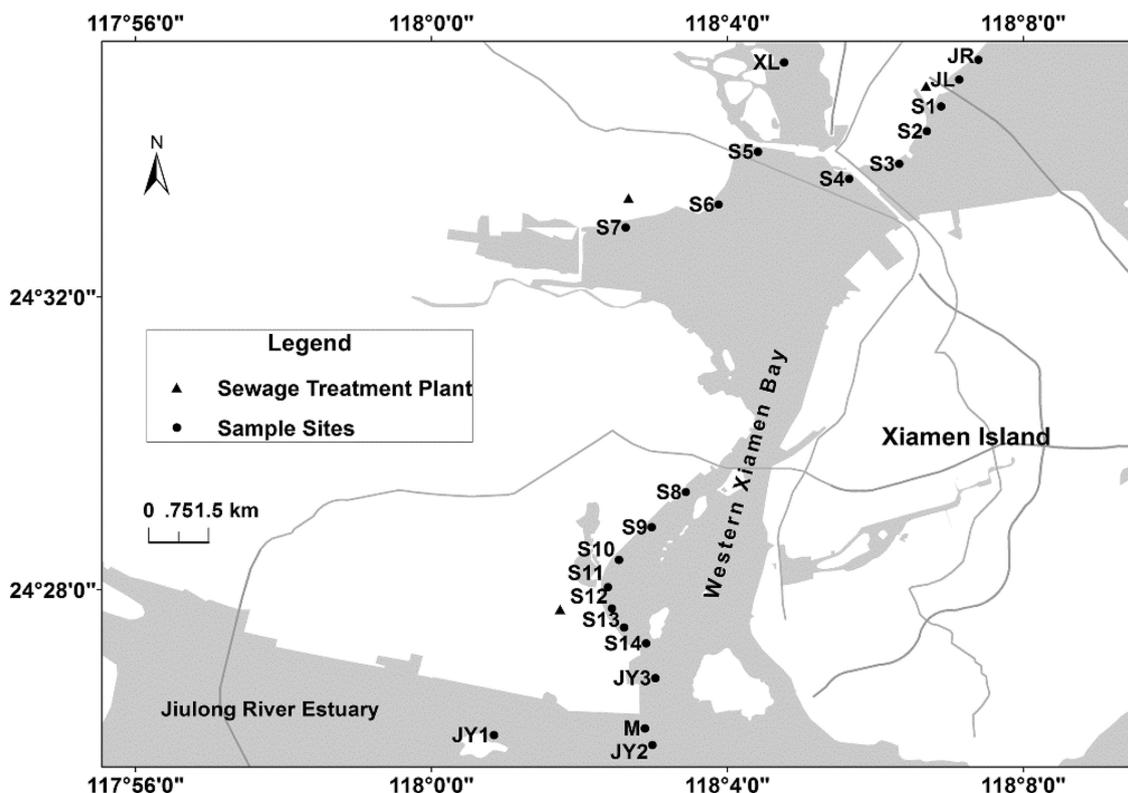

Fig. 1 Offshore surface sediment sampling sites in western Xiamen Bay

plasma-optical emission spectrometry (ICP-OES) (Optima 7000DV, USA), and Hg was determined by atomic fluorescence spectrometry (AFS). Meanwhile, equipment condition monitoring and quality control were performed by measuring a standard solution after every 16 samples. The recoveries of the standard solution were within 85 %–102 %. Recoveries obtained for the studied elements in the reference material were within 73 %–128 %. All the relative standard deviations (CV) of the replicate samples were less than 10 %.

2.4 Analysis of the fractionation of heavy metals

A modified BCR sequential extraction procedure (Yu et al. 2010) was applied to extract different fractions of 14 elements in sites S1 to S14 using the method illustrated in Table 1.

After centrifugation in each of these four steps, the resultant supernatant was transferred to a 50-mL volumetric flask. The residue was washed twice (10 mL per wash) with deionized water, followed by a second centrifugation. The final supernatant was transferred into the same 50-mL volumetric flask mentioned before and diluted to 50 mL with 3 % HNO_3. The solution was stored in a freezer at 4 °C until analysis. The elements were determined from the modified BCR procedure and measured by ICP-OES except Hg, which was measured by AFS.

Quality control of the modified BCR sequential extraction procedure was assured by parallel samples, and the results were tested by recoveries. The recovery of the sequential extraction was calculated as follows:

$$\text{Recovery } (\%) = \frac{\text{F1} + \text{F2} + \text{F3} + \text{F4}}{\text{Total concentration}} \times 100 \quad (1)$$

Results indicate that most of the recoveries were within 70 %–130 % and the RSD values of parallel samples were less than 5 %.

2.5 Data processing

ArcGIS 10.2 was used to construct the sampling sites map. SPSS 16.0 was used for correlation analysis. GraphPad Prism version 6.00 for Windows software was used to plot the graphs.

3 Results and discussion

3.1 Physico-chemical parameters

The main physico-chemical parameters of surface sediments in western Xiamen Bay are shown in Table 2.

The pH of the sediments ranged from 6.43 to 7.30, with a mean value of 6.90. The pH values fluctuated around 7, and the coefficient of variation was 4.15 %, indicating a relatively small difference across the study area. TC and organic matter in the sediments played an important role in heavy metals concentration and distribution. In this study, the TC mean value was 13.96 g/kg, with a range of 7.39–41.42 g/kg and coefficient of variation 48.16 %. The maximum was at site S7, which was near a large discharge outlet and surrounded by domestic garbage. LOI content was between 5.06 % and 10.53 %, with a mean value of 7.99 %. The maximum LOI was also at site S7. TC and LOI were generally high, which might mainly be attributable to the offshore sewage and domestic garbage.

3.2 Distribution and level of total heavy metals in the sediments

Distributions of heavy metals in the offshore surface sediments from western Xiamen Bay are shown in Fig. 2 by sample site. Statistics of concentrations of heavy metals in surface sediments are shown in Table 3, including mean values and CVs of elements from this study's samples, element background values in offshore sediments elsewhere in China, and concentrations of heavy metals in various studies of sediments in China and abroad.

Compared with the sediment element background values in offshore sediments in China, the concentrations of Li, Cr, Co, Cu, Zn, Mn, Pb, Fe, Ti, and Hg were higher; V, Ni, Sr, and Ba were lower than their respective background

Table 1 The modified BCR sequential extraction procedure

Step	Fraction	Nominal target phase(s)	Procedure
1	Acid soluble-extractable	Exchangeable ions and carbonates	1.0000 g sample, 0.11 mol/L CH_3COOH 20 mL, 22 ± 5 °C, shaken at 220 rpm for 16 h, centrifuged at 4000 rpm for 10 min
2	Reducible	Iron and manganese oxyhydroxides	20 mL $NH_2ON·HCl$ (adjusted to pH 1.5 with HNO_3), 22 ± 5 °C, shaken at 220 rpm for 16 h, centrifuged at 4000 rpm for 10 min
3	Oxidable	Organic matter and sulfides	5 mL H_2O_2 (30 %), 2 h at 85 °C, 25 mL CH_3COONH_4 (1.0 mol/L, adjusted to pH 2.0 with HNO_3), 22 ± 5 °C, shaken at 220 rpm for 16 h, centrifuged at 4000 rpm for 10 min
4	Residual	Metals bound in lithogenic minerals	Same as digestion of total amount of heavy metals

Table 2 Physico-chemical parameters of offshore surface sediments in western Xiamen Bay

ID	pH	CaCO₃ (%)	TC (g/kg)	LOI (%)
S1	7.02	0.56	11.37	5.06
S2	6.89	0.91	10.86	6.63
S3	6.89	1.50	13.92	5.93
S4	6.94	1.98	16.01	7.98
S5	7.30	3.07	11.47	7.10
S6	6.93	1.69	17.06	7.57
S7	6.63	0.56	41.42	10.53
S8	7.04	2.07	17.21	7.89
S9	6.53	1.91	13.24	8.07
S10	6.43	0.75	13.34	7.65
S11	6.51	2.35	11.75	6.97
S12	6.59	4.61	11.21	7.05
S13	6.43	1.19	15.32	6.77
S14	6.66	1.94	10.82	7.03
JR	7.05	1.60	12.60	10.18
JL	7.15	1.21	10.29	9.14
XL	7.21	1.34	7.390	8.99
JY1	7.14	3.18	11.90	9.03
JY2	7.19	2.68	10.81	8.38
JY3	7.25	1.86	11.99	9.54
M	7.09	1.88	13.09	10.41
Max	7.30	4.61	41.42	10.53
Min	6.43	0.56	7.39	5.06
Avg	6.90	1.76	13.96	7.99
CV (%)	4.15	52.69	48.16	18.39

values. Notably, the mean value of Hg was three times higher than the background value. Referring to Marine Sediment Quality (GB18668-2002) issued by General Administration of Quality Supervision, Inspection and Quarantine of the People's Republic of China (AQSIQ 2002) and the Marine Functional Zoning in Fujian Province, the sediments in the study area were measured against the primary standard criteria of Marine Sediment Quality. The results show that concentrations of Pb, Cr, and Hg at most sites met primary standard criteria except site S12 for Pb (71.60 mg/kg) and S7 for Cr (764.1 mg/kg); Zn at 17 sites and Cu at seven sites exceeded the primary standard criteria. The mean values of Pb and Cr both met the primary standard criteria.

Table 3 shows that the elements in this study were not totally consistent with previous reports (Yan et al. 2010; Lin et al. 2014). The concentrations of Cr and Cu in this study were higher than those in the study of Lin et al. (2014) and Yan et al. (2010), while Pb values were lower. This is attributed to variations in sampling sites and time. For example, the Lin et al. (2014) and Yan et al. (2010) studies in Xiamen Bay included western Xiamen Bay, the

Jiulong River estuary, and adjacent areas so the average concentrations of heavy metals from that study represent a different geography. In this study, the sampling sites were all offshore, while the sampling sites in western Xiamen Bay in the study of Yan et al. (2010) and Lin et al. (2014) were from the middle of the bay. The concentrations of Hg, Zn, Cu, and Cr in this study were higher than those in the study of Yan et al. (2010), and the concentrations of Cu and Cr were also higher than those in the study of Lin et al. (2014). Considering that there were a lot of sewage outlets along the banks, the differences might suggest the Hg, Zn, Cu, and Cr were from land-based sources, decreasing from the near-offshore to middle of the bay. In contrast, the concentration of Pb was lower in our study than in other studies. Lin et al. (2014) found that the concentration of Pb was highest a little farther away from the estuary. Both these findings support atmospheric deposition as the main source for Pb pollution, which displays a distribution trend opposite that of other heavy metals. Finally, timing might be another factor that influenced the results of heavy metal concentrations. In the studies of Yan et al. (2010) and Lin et al. (2014), the sampling times were in September of 2007 and from October to November of 2011, respectively. We sampled the sediments from January to July, 2013. Normally, concentrations of heavy metals would be expected to increase with time due to accumulation. Thus, timing might be another factor contributing to differences between this study and previous studies.

Compared with other areas in China and abroad, the concentrations of V, Cu, Zn, and Mn in this study were all higher than those in sediments of other areas, like the Yellow Sea (Guo et al. 2011), Jiulong River estuary (Wang et al. 2014), Hongkong (Zhang et al. 2015), Kachemak Bay (Apeti and Hartwell 2015), and Mahshahr Bay (Vaezi et al. 2015). The concentrations of Cr and Pb were lower than those in Hongkong (Zhang et al. 2015); the Hg concentration was lower than that in the Jiulong River estuary (Wang et al. 2014).

In order to determine the distribution of elements and the factors that influenced them, we used SPSS 16.0 to evaluate the correlation among heavy metals and environmental factors. The correlation matrix is given in Table 4. A significant correlation between heavy metals indicates their common origin or similar level of contamination. The correlation matrix shows that Cr, Ni, Cu, and Zn were significantly correlated with each other, indicating they might have similar levels of contamination or a common source. Furthermore, unlike LOI, TC correlated with many elements, such as Cr, Ni, Cu, Zn, V, and Sr, which meant TC influenced the distribution of these heavy metals.

The studied elements can be divided into six patterns (Table 5) according to comparison with the element background values in offshore sediments in China and their variation between sites.
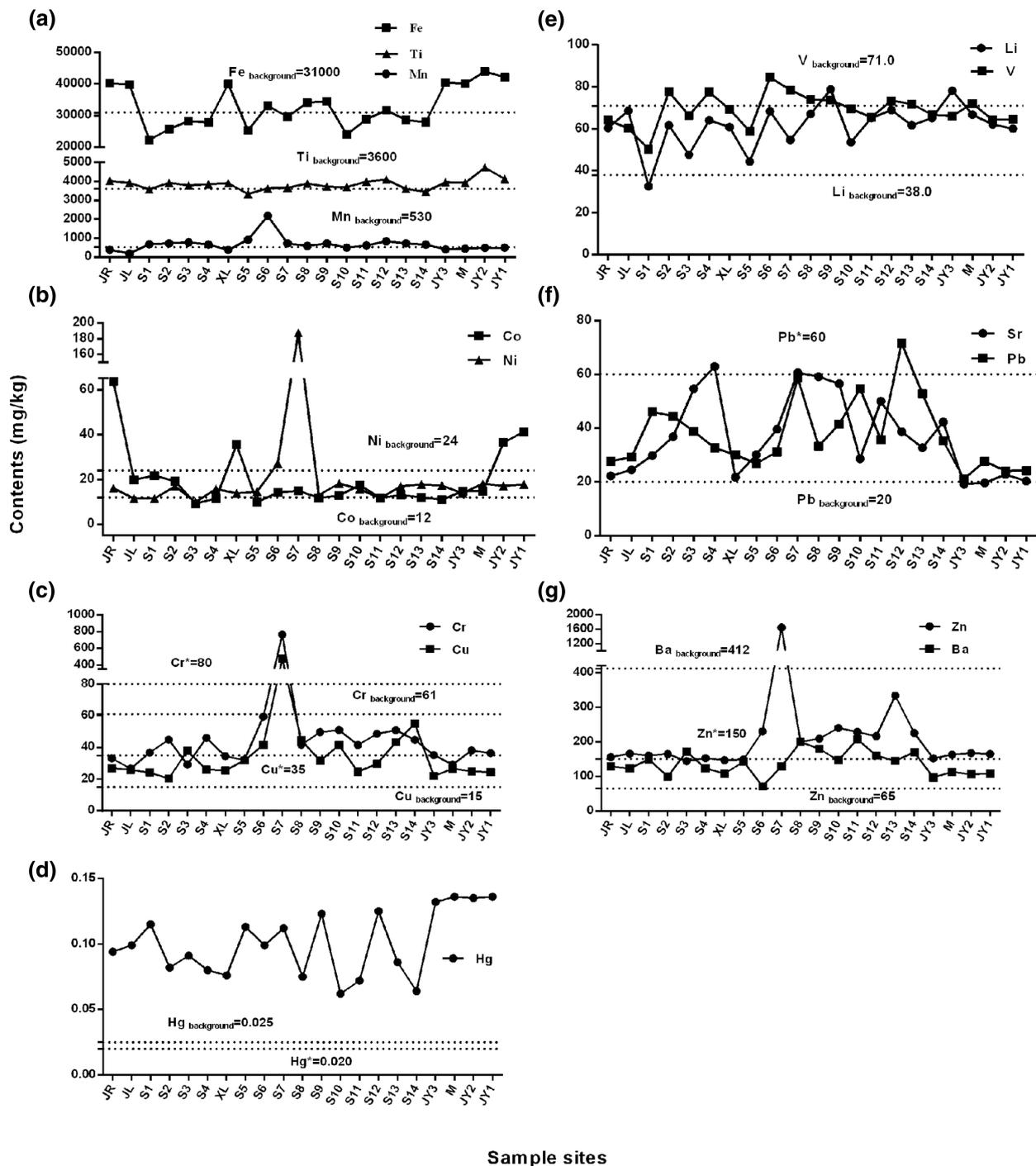
Fig. 2 The distribution of heavy metals in surface sediments: **a** distribution of Fe, Ti, and Mn; **b** distribution of Co and Ni; **c** distribution of Cr and Cu; **d** distribution of Hg; **e** Li and V; **f** Sr and Pb, (the background value of Sr is 230 mg/kg); and **g** distribution of Zn and Ba. The data which are marked with *asterisk* are the primary standard criteria from marine sediment quality (GB 18668-2002) (CSBTS 2002). Data of background values are element background values in offshore sediment in China from Zhao and Yan (1993)

First, Ba (C_{mean} = 131.1 mg/kg) and Sr (C_{mean} = 36.79 mg/kg) levels were far below their respective background values (412 mg/kg for Ba, 230 mg/kg for Sr). Significant correlation between them (r = 0.547, p < 0.05) suggest

that they might be from a natural source. Compared with Ba (CV = 25.07 %), Sr showed a higher variation across sites (CV = 39.83 %) and had a more significant correlation with pH (r = −0.487, p < 0.05) and TC (r = 0.519,

Table 3 Summary of heavy metals mean concentrations in the surface sediments of this study, related surface sediment values from some other areas in China and abroad, background values, and primary standard criteria in Marine Sediment Quality (all mg/kg)

	Li	V	Cr	Co	Ni	Cu	Zn	Sr	Mn	Pb	Ba	Fe	Ti	Hg	Reference
Xiamen, China	61.50	69.04	74.89	19.87	23.93	52.51	257.9	36.79	674.0	37.49	131.1	32,783	3847	0.100	This study
CV (%)	16.85	10.91	206.1	66.31	153.7	180.8	121.7	39.83	55.88	34.04	25.07	19.90	7.34	24.12	This study
Background Value	38.0	71.0	61	12	24	15	65	230	530	20	412	31,000	3600	0.025	Zhao and Yan 1993
Xiamen, China	–	–	34	–	–	39	145	–	–	52	–	29,650	–	0.073	Yan et al. 2010
Xiamen, China	–	–	53.5	–	–	23.4	–	–	–	40.2	–	–	–	–	Lin et al. 2014
Yellow Sea, China	–	–	32.50	–	–	18.84	56.10	–	626.20	17.64	–	27,300	–	0.019	Guo et al. 2011
Jiulong River Estuary	15.55	15.79	31.26	44.68	33.79	26.69	167.3	–	681.3	27.65	474.7	43,473	2598	0.14	Wang et al. 2014
Kachemak Bay, USA	–	–	76.7 ± 2.6	–	38.9 ± 1.01	35.6 ± 2.6	95.1 ± 4.4	–	649 ± 29	11 ± 0.4	–	40,800 ± 1200	–	0.09 ± 0	Apeti and Hartwell 2015
Mahshahr Bay, Persian Gulf	–	–	70 ± 5.4	–	29.7 ± 0.34	26.5 ± 0.001	183.4 ± 1.4	85 ± 3	488 ± 4	–	300 ± 3.2	–	–	–	Vaezi et al. 2015
Hongkong, China	–	29.9	33	–	20.2	37.3	119	–	546.6	43.2	30.2	27,628	–	–	Zhang et al. 2015
Marine sediment quality (primary standard criteria)	–	–	80	–	–	35	150	–	–	60	–	–	–	0.20	AQSIQ 2002

Background Value refers to element background values in offshore sediments in China (Zhao and Yan 1993)

– not available

Table 4 Matrix of Pearson correlation coefficients among heavy metals and physico-chemical parameters of the offshore surface sediments (n = 21)

	Li	V	Cr	Co	Ni	Cu	Zn	Sr	Mn	Pb	Ba	Fe	Ti	Hg	pH	CaCO$_3$	TC	LOI
Li	1																	
V	.516*	1																
Cr	−.132	.317	1															
Co	−.074	−.277	−.099	1														
Ni	−.112	.341	.997**	−.078	1													
Cu	−.146	.304	.996**	−.118	.993**	1												
Zn	−.116	.325	.994**	−.128	.990**	.993**	1											
Sr	.054	.471*	.384	−.542*	.355	.394	.385	1										
Mn	−.017	.493*	.066	−.326	.097	.066	.074	.293	1									
Pb	−.176	.267	.395	−.337	.369	.389	.438*	.363	.139	1								
Ba	−.086	−.206	−.051	−.353	−.100	−.017	−.010	.547*	−.204	.328	1							
Fe	.540*	−.018	−.129	.566**	−.094	−.140	−.151	−.481*	−.309	−.573**	−.400	1						
Ti	.319	−.018	−.155	.506*	−.147	−.191	−.180	−.281	−.349	−.232	−.222	.677**	1					
Hg	.102	−.179	.092	.164	.124	.061	.060	−.356	−.024	−.163	−.360	.496*	.366	1				
pH	−.107	−.362	−.250	.380	−.228	−.256	−.323	−.487*	−.162	−.756**	−.510*	.522*	.269	.393	1			
CaCO$_3$	.282	−.023	−.304	.004	−.291	−.312	−.310	−.063	.077	−.048	.142	.275	.353	.397	.122	1		
TC	−.091	.441*	.944**	−.196	.944**	.947**	.946**	.519*	.205	.368	−.004	−.176	−.211	.052	−.289	−.311	1	
LOI	.447*	.216	.378	.428	.410	.368	.353	−.266	−.334	−.337	−.406	.719**	.322	.332	.301	−.019	.335	1

* Correlation coefficients at 95 % significance level (p < 0.05)

** Correlation coefficients at 99 % significance level (p < 0.01)

Table 5 Six patterns of fourteen elements concentration	CV	<Background		≈Background		>Background	
		Low	High	Low	High	Low	High
	Element	Ba	Sr	Fe, V, Ti	Mn, Ni, Cr	Li, Pb, Hg	Co, Cu, Zn
	Abnormal data (mg/kg)				Ni (S7) = 187.6		Cu (S7) = 475.3
					Cr (S7) = 764.1		Zn (S7) = 1648

p < 0.05), indicating that Sr might be more easily influenced by physico-chemical conditions.

Second, Ti, Mn, Ni, Cr, Fe, and V values were comparable to their background values. More specifically, Ti, Fe, and V varied less between sites compared with Mn, Ni, and Cr, except for site S7 where Ni concentration was 187.6 mg/kg and Cr concentration was 764.1 mg/kg. All concentrations of Ni and Cr were below their background values except sites S6 and S7 for Ni, and site S7 for Cr. Ni and Cr were highly correlated (r = 0.997, p < 0.01), showing that they might have the same origin. High concentrations of Ni and Cr might have resulted from high TC at site S7 (TC = 41.42 g/kg), since strong correlations were found between Ni, Cr, and TC: Ni-TC (r = 0.944, p < 0.01), Cr-TC (r = 0.944, p < 0.01). Site S7 was located in the coastal area of Xingbin Road, where there was a large sewage treatment plant nearby (see Fig. 1) and 60 % of the sewage was industrial effluents which caused high TC, resulting in an increase of accumulated elements. Mn concentrations in site S6 were three to four times that of other sites, showing that point pollution sources of Mn existed. The high variation of Fe and V might be because of the differences between sites. Fe showed significant correlation with pH and LOI: Fe-pH (r = 0.522, p < 0.05), Fe-LOI (r = 0.719, p < 0.01). V correlated significantly with TC (r = 0.441, p < 0.05).

Third, concentrations of Co, Cu, Zn, Li, Hg, and Pb were higher than their background values, indicating that they might be affected by an anthropogenic source. Li, Hg, and Pb showed less variation between sites compared with Co, Cu, and Zn, except site S7 (475.3 mg/kg for Cu, 1648 mg/kg for Zn). Cu and Zn were strongly correlated with each other (r = 0.993, p < 0.01). Moreover, Cu, Zn, Ni, and Cr were strongly correlated with each other (r > 0.99, p < 0.01), indicating that they might be from the same sources. High concentrations of Cu and Zn might be due to high TC at site S7, as strong correlations were found between Cu and Zn, and TC: Cu-TC (r = 0.947, p < 0.01), Zn-TC (r = 0.946, p < 0.01). Li and Pb concentrations changed erratically between sites. Significant correlation can be seen between Li and LOI (r = 0.441, p < 0.05), Pb and pH (r = −0.756, p < 0.01). Notably, the mean value of Hg was three times higher than the background value, indicating an obvious anthropogenic source. Relatively high concentrations of Hg were found at sites S1, S7, and

S12 where there were sewage treatment plants nearby. That suggests Hg might partly come from sewage fallout. Hg concentration was also high at sites S5 and S9. More important, Hg showed high concentration at sites JY1, JY2, JY3, and M which were near the Jiulong River estuary. Hg reached its maximum at site JY1, which might be related to the site's proximity to the Jiulong River.

3.3 Fractionation of heavy metals in sediments

A modified BCR sequential extraction method was used to extract the heavy metals in sites S1 to S14 to obtain measure fractionation concentrations. The results are shown in Fig. 3. According to the differences between sampling sites, elements can be divided into three categories.

The first category included Fe, Ti, Ba, Co, V, and Li, dominated by the residual phase at all sites with average proportions of 74.96 %, 99.82 %, 76.73 %, 76.00 %, 89.94 %, and 83.08 %, respectively. The distribution of the different fractions showed small differences between sites for these elements. Other studies also reported that these elements mainly existed as the residual fraction in sediments (Wang and Zhang 1999; Yu et al. 2008). The residual fraction mainly existed in mineral crystal form, and cannot be used by organisms; they may be regarded as a natural source contribution (Davutluoglu et al. 2010). Fe, Ba, and Co were similar in their proportion of the reducible fraction (F2), accounting on average for 16.69 %, 22.96 %, and 17.42 %, respectively. But, as mentioned above, the total concentrations of Ba and Fe did not exceed the background values. Though Co was above the background value, it was dominantly in the residual fraction. Fe, Ti, Ba, Co, V, and Li in the coastal sediments of western Xiamen Bay were mainly from terrestrial input.

The second fractionation category included Ni, Cr, Pb, and Hg, also dominated by the residual phase. However, concentrations of these elements in the non-residual phases (F1, F2, and F3) showed large differences between sites. At site S7, the non-residual phase concentrations of Cr and Ni were particularly high, indicating anthropogenic sources. This might be because site S7 was near the sewage treatment plant, and thus polluted by the sewage. The residual proportions of Pb and Hg were 47.48 % to 74.09 % and
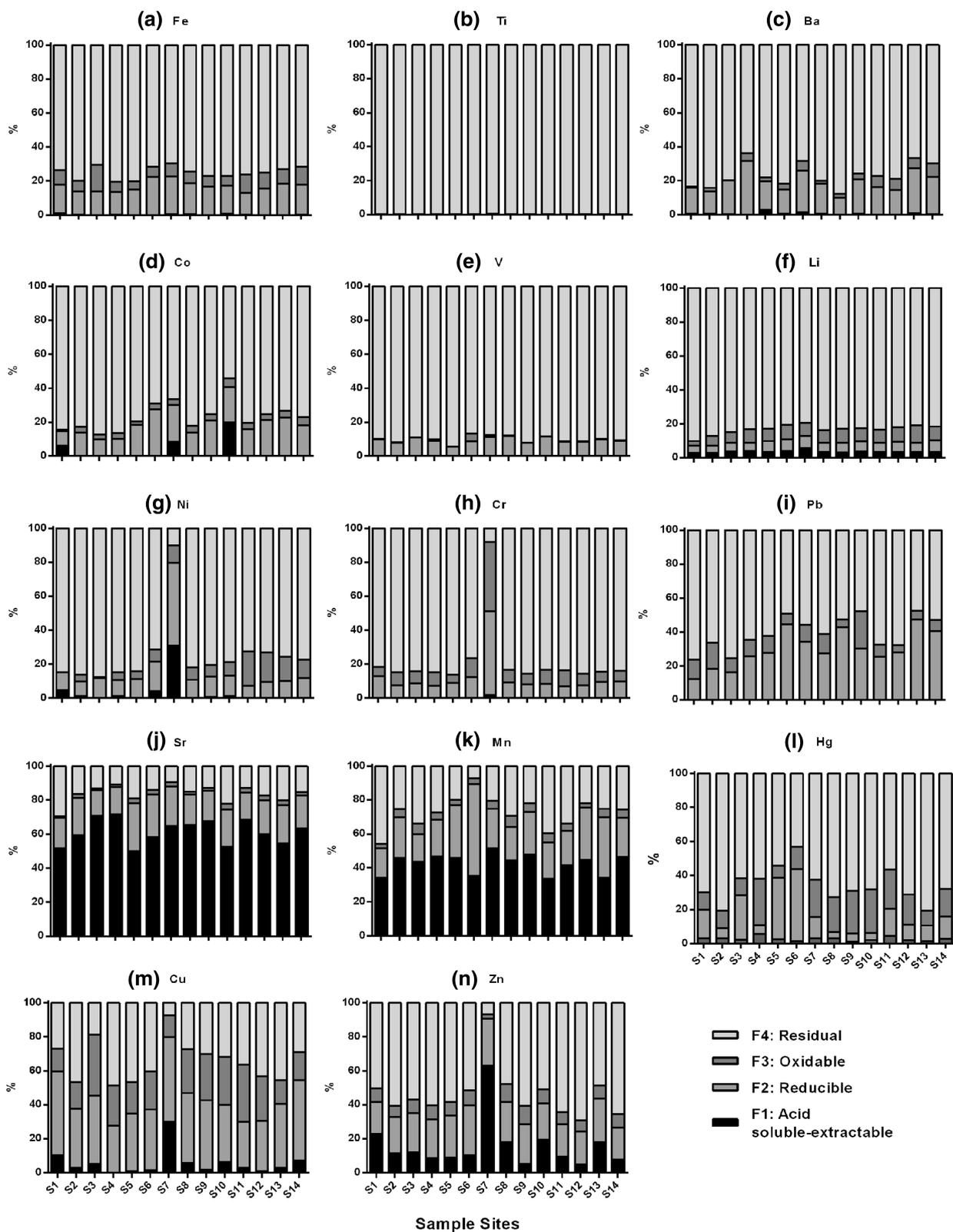
Fig. 3 Percentage of fractionation of heavy metals at sites S1 to S14 in surface sediments

43.10 % to 80.77 %, respectively, indicating that Pb and Hg also occurred mainly in the residual phase. But the proportion in the non-residual phase was 23.91 % to 51.52 % for Pb, and 19.23 % to 56.90 % for Hg, indicating that Pb and Hg had also been affected by anthropogenic sources.

The third category included Sr, Mn, Cu, and Zn, for which the non-residual phases dominated. Changes in Zn and Cu were not regular, which might be because in addition to physical and chemical conditions, they were also influenced by human interference. Sr and Mn distributions were more stable. It is worth noting that the non-residual phases of Zn and Cu were abnormally high at site S7, like Cr and Ni. In addition, the total concentrations of Zn, Cu, Cr, and Ni exceeded the background values, which proved there were anthropogenic sources attributing heavy metals to site S7.

The average proportions of the non-residual phases of Zn, Cr, Cu, and Ni were 62.3 %, 56.32 %, 77.31 %, and 51.05 %, respectively, indicating Zn, Cr, Cu, and Ni had high mobility and bioavailability. Guo et al. (1997) suggested that Zn and Cr are mainly influenced by redox potential and are bound to Fe–Mn oxides in an oxidizing condition. In the exchangeable and carbonate, or Fe–Mn oxide phase, heavy metals might be easily released into the environment, producing a higher potential risk. Cu, as a chalcophile element, can form organic complexes and copper sulfide with organic acid molecules through chelation, but it is also affected by the adsorption of Fe–Mn oxides (He et al. 2010).

Acid soluble-extractable Sr and Mn were high at all sample sites. The mean proportional order of the phases is F1 > F2 > F4 > F3. Sr is a biogenic element, mainly accumulating in bioclastic-containing calcium carbonate, so a high proportion of Sr presents in the exchangeable and carbonate phase. Mn is also mainly in the exchangeable and carbonate phase. Chen et al. (1987b) found nearly half of Mn was in the acid-soluble phase in surface sediments of Xiamen Harbor. Mn concentration may be partly due to ocean authigenesis in the sediments of Xiamen Bay, coupled with the impact of a high MnO concentration in adjacent rocks, leading to most Mn occurring in the extractable phase (Qian 2001).

3.4 Pollution assessment of heavy metals in the sediments

We used potential ecological risk index (RI) and the ratio of secondary phase to primary phase (RSP) to assess the degree of heavy metal pollution in sediments, in order to understand the sediment quality better.

3.4.1 Potential ecological risk assessment

Håkanson (1980) developed a method that had been widely introduced to assess ecological risks of heavy metal pollution in sediments (Fernandes 1997; Yang et al. 2009; Zhu et al. 2012). The calculating formulas are as follows:

$$RI = \sum E_r^i \qquad (2)$$

$$E_r^i = T_r^i \cdot C_f^i \qquad (3)$$

$$C_f^i = C_0^i / C_n^i \qquad (4)$$

$$C_d = \sum C_f^i \qquad (5)$$

where RI is the requested potential ecological RI for the sediments, E_r^i is the potential ecological risk factor of the given pollutant (i), and T_r^i is the "toxic-response" factor of the given pollutant (i). In this paper, the T_r^i values were taken as Hg = 40, Mn = Zn = Ti = 1, V = Cr = 2, and Co = Ni = Cu = Pb = 5 (Xu et al. 2008). C_f^i is the contamination factor of the given pollutant (i), and C_d is the comprehensive contamination degree of all the studied pollutants. C_0^i is the measured concentration of the given pollutant (i) in the sediments, and C_n^i is the standard preindustrial reference level of i. In this study, we used the element background values in offshore sediments in China (Zhao and Yan 1993).

The number and the kind of pollutants in this paper are both different from those in Håkanson's literature (PCB, Hg, Cd, As, Pb, Cu, Cr, and Zn), therefore the criteria of RI values should be adjusted. Take the first class of RI limits for example; the sum T_r^i in Håkanson's literature is 133, corresponding to an RI limit of 150. In this paper, since the sum T_r^i is 67, the corresponding RI limit is 150 × (67/133) ≈ 75.56 (herein taken integer 75). The criteria for E_r^i and the adjusted criteria for RI are listed in Table 6.

Table 6 Degrees of contamination and potential ecological risk corresponding to the values of E_r^i and RI

E_r^i	Potential ecological risk for single regulator	RI	Ecological risk for all factors
<40	Low	<75	Low
40–80	Moderate	75–150	Moderate
80–160	Considerable	150–300	Considerable
160–320	High	≥300	Very high
≥320	Very high		

Using Eqs. (2) through (5), the potential ecological risk factors, E_r^i, for each element and RI for each site were obtained and plotted in Fig. 4. The results show that the mean values of E_r^i of V, Cr, Co, Ni, Cu, Zn, Mn, Pb, and Ti were all below 40 in the offshore surface sediments of western Xiamen Bay except Cu at site S7, indicating a low ecological risk. However, E_r^i values of Hg were between 99.2 and 217.6, indicating a considerable-to-high ecological risk. E_r^i values decreased in the following sequence of Hg > Cu > Pb > Co > Ni > Zn > Cr > V > Mn > Ti, with Hg contributing 75.89 % of the total RI (Fig. 5). RI values suggest considerable ecological risk at most sites except site S7 (very high), and sites S10, S11, and S14 (moderate). Site S7 is located in the coastal area of Xingbin Road, Xiamen, where there was a large sewage treatment plant nearby (Fig. 1) and 60 % of the sewage was industrial effluent, causing high TC and accumulating high element concentrations.

Above all, results of the potential ecological risk assessment show that heavy metals in the offshore surface sediments of western Xiamen Bay had a considerable potential ecological risk at most sites.

3.4.2 Ratio of secondary phase to primary phase concentrations

RSP can be used to distinguish between anthropogenic sources and natural sources of heavy metals. Thus RSP can reflect the bioavailability and chemical activity of heavy metals and be used to evaluate possible ecological risk. Chen et al. (1987a) named metals in the primary material crystal (residual phase) as the primary geochemical phase, and the non-residual phases (including exchange, carbonate, hydrated Fe–Mn oxides, and organic phases) as the secondary geochemistry phase. The higher the proportion
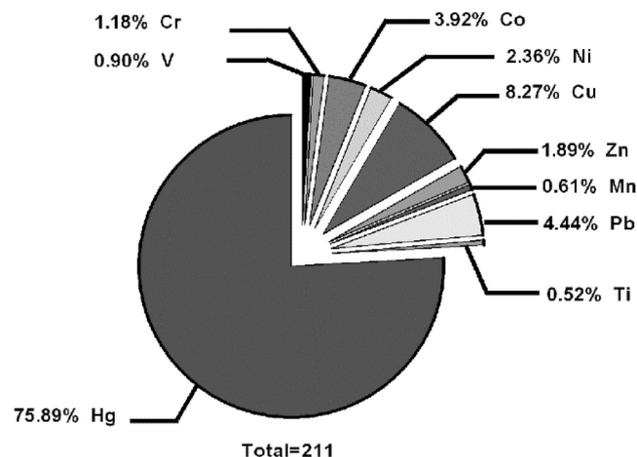
Fig. 5 The contribution of different heavy metals to potential ecological risk index in the sediments

of the secondary phase, the greater the likelihood of heavy metal pollutants released into the environment, and the greater the potential harm (Wang et al. 2012).

The RSP formula is as follows:

$$RSP = \frac{M_{sec}}{M_{prim}} \qquad (6)$$

where M_{sec} is the heavy metal concentration in the secondary phase and M_{prim} is the heavy metal concentration in the primary phase. The relationship of pollution degree and the values of RSP is: RSP < 1, unpolluted; 1 < RSP < 2, low; 2 < RSP < 3, moderate; 3 < RSP, high. The results are showed in Fig. 6.

The average RSP values for Sr and Mn were 5.70 and 4.71, respectively. But Sr and Mn are biogenic elements, mainly enriched in the calcium carbonate debris, and the total concentration of Sr was lower than the background
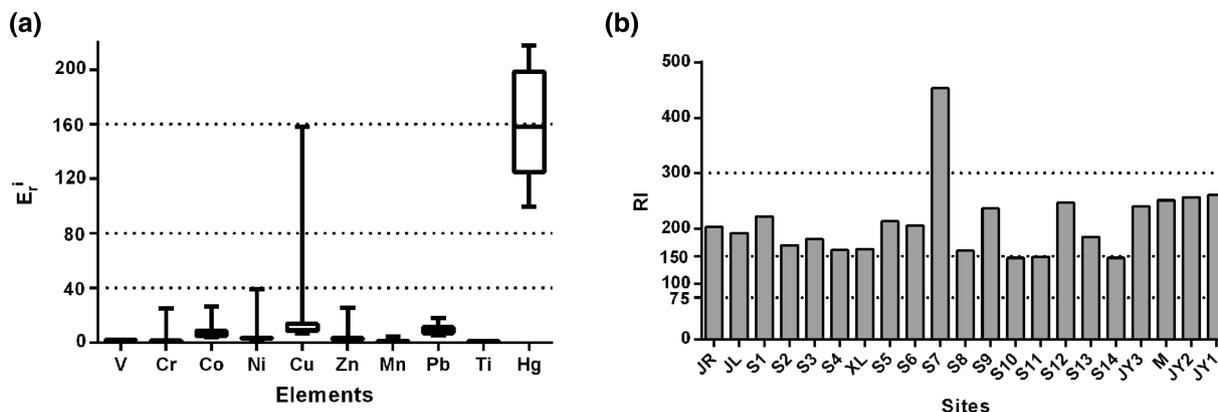
Fig. 4 The potential ecological risk coefficients and risk indices of heavy metals: **a** E_r^i value of each metal in the studied area. Boxes extend from the 25th to 75th percentiles. *Lines* in the middle of the boxes are plotted at the medians. The whiskers go down to the smallest values and up to the largest. **b** RI value of the studied metals for each site
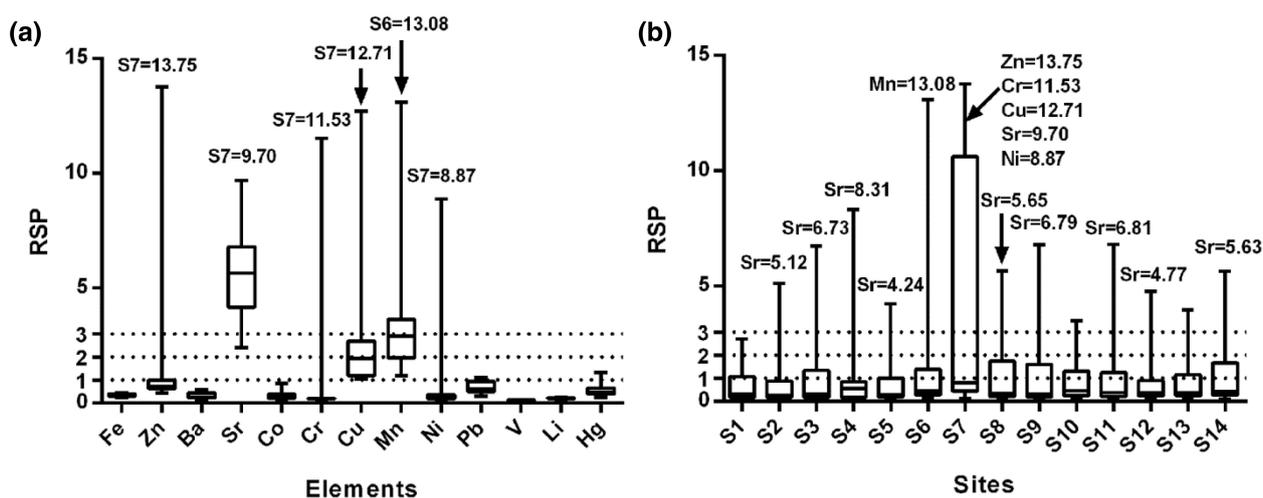
Fig. 6 The RSP of heavy metals in surface sediments: **a** RSP value of each element in the studied area. **b** RSP value of the studied elements for each site. Boxes extend from the 25th to 75th percentiles. *Lines in the middle of boxes* are plotted at the median. The whiskers go down to the smallest values and up to the largest

value, while the total concentration of Mn was comparable with the background value. Therefore, it is not appropriate to assess these elements using the RSP method. The RSP of Cu was between 1.6 and 4, indicating low-to-high pollution. The RSPs of Zn, Cr, Cu, Ni, and Sr all showed the largest values at site S7 (Fig. 6a). But aside from the site S7 outliers, RSP values of Cr and Ni were between 0 and 1, indicating an unpolluted condition. In contrast to the results of RI, RSP of Hg was between 0 and 1, except at site S6 (1.32), also indicating an unpolluted condition. This is because Hg mainly existed in the residual fraction (Fig. 3). Most RSP values of Zn and Pb were between 0 and 2, while RSP values of Fe, Ba, Co, V, and Li were less than 1 at all sampling sites. Overall, Cu showed low-to-high pollution or bioavailability and chemical activity. Pb and Zn registered as no-to-low pollution, while other metals were found to be at non-pollution levels. Consistent with the results of RI, site S7 was heavily polluted by Zn, Cr, Cu, and Ni. The RSP values at other sites were mostly between 0 and 2, meaning low-to-moderate pollution (Fig. 6b), except for Sr with RSP values between 2.40 and 9.70 and Mn with an RSP of 13.08 at site S6.

There were differences between the results of RI and RSP. For example, the RI method showed that Hg presented a considerable-to-high ecological risk, but an unpolluted condition using the RSP method. One of the reasons is that the method of RSP does not take the background value and toxicity of heavy metals into consideration, but is only based on the relative proportion of fractions. RSP can be seen as a method to assess the bioavailability and chemical activity of heavy metals. It is better to use both methods to assess the contamination of heavy metals.

4 Conclusions

In order to study the distribution, contamination level, bioavailability, and chemical activity of heavy metals in the offshore surface sediments collected from western Xiamen Bay, total concentrations and four fractions of heavy metals were determined to assess the pollution and potential ecological risk degree of heavy metals using RI and RSP methods.

Concentrations of Pb, Cr, and Hg at most sampling sites met the primary standard criteria of Marine Sediment Quality (GB18668-2002) except Pb at site S12 and Cr at S7. The mean concentration of Zn was 257.90 mg/kg, and Cu was 52.51 mg/kg. Notably, the mean concentration of Hg was three times higher than the background value, indicating an obvious anthropogenic source, which might be contributed primarily by the Jiulong River. Fe, Ti, Ba, Co, V, and Li were dominated by the residual phase, and were mainly from terrestrial input. The non-residual phases of Ni, Cr, Pb, and Hg showed large differences between sites, and have been affected by anthropogenic sources. Sr, Mn, Cu, and Zn were dominated by the non-residual phases. Zn and Cu were also influenced by human interference, while Sr and Mn mainly originated from ocean bioclasts and authigenesis, coupled with adjacent rocks. We used RI to assess the pollution degree of total heavy metals and RSP to assess the bioactivity of heavy metals in sediments. According to the assessment results of potential ecological risk, the heavy metals at most sampling sites had a considerable ecological risk except for site S7 (very high) and sites S10, S11, and S14 (moderate). With respect to RSP, Cu showed moderate-to-high pollution. Pb exhibited no-to-

low pollution status, while other metals registered as unpolluted. Results of the above assessment methods indicate that there was moderate pollution at site S7 by Cu, Zn, Ni, and Cr and a very high ecological risk, which might be because of the local sewage treatment plant.

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