CONTAMINATION, RISK ASSESSMENT OF HEAVY METALS IN SURFACE SEDIMENTS FROM A MARICULTURE BAY IN SOUTH CHINA

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Abstract. In order to assess the contamination, ecological and biotoxicity risk of heavy metals (Cd, Cr, Cu, Ni, Pb and Zn) in mariculture area of China, the total concentrations and speciation of metals were analysed in the sediments from a typical mariculture bay in 2011 and 2013. The results show that most heavy metal concentrations in 2013 were lower than those in 2011. The residual and sulfide-bound fractions were the primary fractions of heavy metals. The pollution can be described in all the sampling sites of heavy metals (except Cd) with moderate to a very high degree by geo-accumulation index (Igeo), enrichment factor (EF) and pollution load index (PLI). According to the risk assessment code (RAC), Cd, Ni and Pb posed a medium to very high ecological risk. The sampling sites that exhibited the biotoxicity risk in 2013 had higher biotoxicity levels than that in 2011. Based on statistical analysis and environmental investigation, four sites (S1, S2, S4 and S7) were highly affected by the environmental pollutants which primarily resulted from the combustion of gasoline and diesel fuel and the ships protective layer.

Keywords: ecological risk, biotoxicity risk, Zhelin Bay, speciation, pollution load index, the risk assessment code

Introduction

Heavy metals in ecosystems have received extensive attention because they are toxic, non-biodegradable, and easily bioaccumulate in organisms (Al-Othman et al., 2012; Dabney et al., 2018; Gao et al., 2012; Ghosh et al., 2018; Islam et al., 2014; Väänänen et al., 2016; Yang et al., 2012). With rapid industrialization and economic development in the coastal region of South China, heavy metals from industrial waste, sewage runoff, and agricultural discharges, are continuously introduced into the estuarine and bay environment through rivers, runoff, dust deposition and land-based point sources (El Nemr et al., 2016; Hyun et al., 2007; Wu et al., 2015; Yu et al., 2008). Due to the adsorption, hydrolysis, and co-precipitation of heavy metals, most of such pollutants deposit in the sediments and only a small part of free metal ions leave in water (Chaudhary et al., 2015; Hu et al., 1997; Nobi et al., 2010; Zwolsman et al., 2013.)

In recent decades, various assessment indices have been applied to assess the environmental pollution and risk of heavy metals in marine sediments. The heavy metal contamination in sediments is evaluated by the geo-accumulation index (Igeo), enrichment factor (EF) and pollution load index (PLI) (Gu et al., 2018; Liu et al., 2014; Varol et al., 2011; Wang et al., 2016;). In particular, the Hakanson risk index is prevalent in evaluating the ecological risk posed by heavy metals in sediments (Wu et al., 2014; Yi

et al., 2011; Zhuang et al., 2014.). However, the mobility and toxicity of heavy metals in sediment depend not only on their total concentrations, but also on their physicochemical fractions described as "speciation" (Yuan et al., 2004; Zhou et al., 2004.). The sequential extraction (SE) technique is often used to determine heavy metal speciation in sediments, defined operationally as acid soluble, reducible, oxidizable and residual fractions (Gao et al., 2010; Zhang et al., 2013.). Meanwhile, sediment quality guidelines (SQGs) and acid volatile sulfide (AVS)-simultaneous extracted metals (SEM) model are widely applied to analyze the bio-toxicity of heavy metals (Prica et al., 2008; Poot et al., 2009; Sundaray et al., 2011.). The exchangeable and carbonate fractions are usually used in the method of the risk assessment code (RAC) to assess the ecological risk.

Zhelin Bay, a semi-enclosed estuarial bay, which situated in the northeast part of Guangdong Province, is one of the most developed areas in China. Zhelin Bay is the largest cage mariculture areas and a vital culture fish zone in South China (Qiao et al., 2010) with many seaport container terminals for international seafood export. Due to the maritime activities, a lot of phosphorus, nitrogen, and organic wastes are discharged, and consequently result in water eutrophication (Cao et al., 2007; Liang et al., 2011; Wu et al., 2016; Xia et al., 2016). Meanwhile, the heavy metal pollution in the bay area is getting worse (Qiao et al., 2010; Xia et al., 2016). The high concentration of heavy metals in sediments can be directly or indirectly bio-accumulated in benthic invertebrates, as sediments provide the benthic fauna food sources and habitats. Therefore, the environmental hazards in the bay become increasingly severe (Kalantzi et al., 2013). The risk assessment of heavy metals in the sediment of the culture area has gained much attention because of the pollution characteristics and ecological hazards of heavy metals.

Our previous study suggested that the ecological risk level of heavy metals in this area is medium to high, especially at the northwest coastal area of the semi-closed bay (Wang et al., 2016). This study was conducted to consolidate and complement the previous results. PLI was used to assess the metal contamination compared with the EF and I_{geo} results. Based on heavy metal speciation, RAC was used to assess the ecological risk, and the results were compared with the Hakanson risk index. The AVS-SEM model was used to predict the bio-toxicity risk, and the results were compared with the SQGs. The study aims to analyze and evaluate the pollution and risk of heavy metals in this area, and identify the potential sources of high risk. The results could provide crucial information for the monitoring, management and conservation of coastal environments.

Materials and methods

Sampling

Samples of surface sediment from eleven sites were collected using a Petersen grab in September 2011 and August 2013 (*Fig. 1*) from Zhelin Bay in southern China. Temperature, salinity, pH and dissolved oxygen of the bottom water were measured by YSI water quality sensors on site (600R mode, YSI Inc., USA). Triplicate sediment samples were placed in the N_2 filled polypropylene bags rapidly after collection, immediately transported to the laboratory and freeze-dried before chemical analysis.

Chemical analysis

After drying at 70 °C for more than 24 h, the samples were re-weighted for the determination of moisture. Sediment total organic carbon (TOC) contents were estimated

by the wet oxidation method using K₂Cr₂O₇ -H₂SO₄ (Mingorance et al., 2007). The total concentration of heavy metal in sediment samples was analyzed following the EPA 3052 method (Wang et al., 2011). The concentrations of Al, Fe, Mn, Si, Cu, Ni, Pb, Zn, Cr and Cd in the final solutions were measured by microwave plasma-atomic emission spectroscopy (MP-AES, Agilent 4200) and atomic absorption spectrometry (AAS, Hitachi Z-2000). Analytical accuracy was achieved by the use of blanks and certified reference materials including GBW 07314 and GBW 07334, issued by the State Oceanographic Administration of China.



Figure 1. The study area and sediment sampling sites in Zhelin Bay along the southern coast of China

Extraction operations were performed by rotary shaking at 20 °C in dark environment with 100 ml of sealed centrifuge tubes. By centrifuging (4000 rpm, 10 min), the separation of the solid from solution was carried out for each step. The supernatant was then thrown away, and the residual was rinsed and centrifuged again. The centrifuge tubs were filled with N_2 in the experimental procedure. After acidifying the metal solutions with HNO₃, the metal concentration was determined by MP-AES and graphite furnace atomic absorption spectrometry (GFAAS, Thermo SOIAAR M6).

Five fractions from 4.5 g wet sediment were extracted using the proposal sequential extraction (PSE) procedure (Wang et al., 2011; Xia et al., 2016). Five fractions were weak acid soluble fraction (F1: pH 5.0, 1 M NaOAc, sample dry weight/extractant volume (SE) 1:15, 5 h), reducible fraction (F2: pH 2.0, 0.2 M NH₂OH•HCl + 0.2 mM EDTA-Na₂, SE 1:15, 5 h), organic matter bound fraction (F3: pH 9.8, 0.1 M Na₄P₂O₇, SE 1:10, 5 h), sulfide bound fraction (F4: 6 M HCl, SE 1:10, 1 h) and residual fraction (F5: estimated as the total metal content). F1 was the bioavailable fraction of heavy metals including the exchangeable and carbonates bound fractions.

The procedure for AVS analyses was protected by N_2 and the same with that by Allen et al. (1993). The suspension in the acidified sediment was filtrated with a 0.45 μ m membrane filter (Fang et al., 2005) and analyzed by MP-AES and GFAAS. Standard materials validated the results. By methylene blue method, the sulfide in the trapping solution was analyzed.

Ultra-pure, deionized water (Milli-Q) was boiled and purged with nitrogen to remove dissolved oxygen. All glassware and plastic containers were soaked in 2.7 M HNO₃ for at least 24 h and rinsed with deionized water before use. Standard solutions were prepared by dilution of 1000 μ g/mL stock solutions with deionized water. All chemicals used in the experiment were at least of analytical reagent grade (p. A.) or superior purity. The concentrations of sediment components, including AVS, TOC, and metals were expressed as dry weight normalized concentrations.

Assessment of the metal contamination

The index of contamination factor (CF) and the pollution load index (PLI) were used to describe the sediment quality. PLI of the six metals were counted (Islam et al., 2015). The PLI was defined as the nth root of the multiplications of the CF of metals.

$$PLI = (CF_1 \times CF_2 \times CF_3 \times ... \times CF_n)^{1/n}$$
(Eq.1)

where $CF_{metals} = C_{metal} / C_{background}$.

The background values of Cd, Cr, Cu, Ni, Pb and Zn in sediment were 0.15, 28.6, 15.8, 14.8, 32.2 and 57.8 ug/g, respectively (Qiao et al., 2009; Wang et al., 2010). PLI evaluated the overall contamination evaluation for all sites and a contribution consequence of the six metals. Therefore, the PLI value of zero indicated excellence, 1.0 represented only baseline level pollutants, and more than 1.0 indicated gradual deterioration of estuarine environment (Tomilson et al., 1980). The contamination factor (CF) of a given metal was calculated as the ratio of its measured concentration to natural abundance. The CF was then classified into four grades for monitoring the pollution from each metal over a period of time: low degree (CF < 1), moderate degree ($1 \le CF < 3$), considerable degree ($3 \le CF < 6$), and very high degree (CF ≥ 6). Thus, the CF values indicated the enrichment of each metal in sediments over a period of time (Islam et al., 2015).

Assessment of risk

Assessment of ecological hazardous risk

In order to assess the risk to the ecological environment, the RAC was applied (Perin et al., 1985; Zhao et al., 2012), which was defined as *Equation 2*:

$$RAC = \frac{[M]_{Weak}}{[M]_{Total}} \times 100\%$$
(Eq.2)

where [M]_{Weak} was the concentration of metals in weak acid soluble fraction, and [M]_{Total} was the total concentration of metals. According to the RAC values, each sample falled into one of the five tiers: i) RAC $\leq 1\%$ (no risk); ii) $1\% < RAC \leq 10\%$ (low risk); iii) $10\% < RAC \leq 30\%$ (medium risk); iv) $30\% < RAC \leq 50\%$ (high risk); v) 50% < RAC (very high risk).

Assessment of biotoxicity risk

The concentrations of AVS, SEM and TOC were used to predict the toxicity (Di Toro et al., 2005). If (\sum SEM-AVS)/ f_{OC} was less than 150 µmol/ g_{OC} , adverse effects due to SEM metals were not expected, and if (\sum SEM-AVS)/ f_{OC} was over than 3400 µmol/ g_{OC} , suggested acute toxicity, and the range of uncertain effects was 150-3400 µmol/ g_{OC} (McGrath et al., 2002).

Quality control and data analysis

The AVS, SEM and speciation analysis in replicates were measured to estimate the precision of the method. The relative standard deviation was less than 12% with the recoveries within 10% for the certified values. Total recoveries as the sum of individual metal fractions from SE compared to total contents were reasonable and ranged from 92.5-110% for Cd, 90.0-112% for Cu, 93.4-110% for Ni, 90.5-108% for Pb, and 96.9%-104% for Zn, respectively.

In this work, factor analysis and correlation analysis were used to elucidate the relationship between metals, parameters and risks, characterize the associated components of heavy metals, and identify the sources of heavy metal contamination. Correlation analysis was performed with two-tailed Pearson test, with p < 0.05 and p < 0.01 as the significant values. The descriptive statistics were used by SPSS 19.0.

Results and discussion

Distribution of heavy metals in the sediments

Among all sampling sites, no fluctuation was observed in the values of pH, dissolved oxygen (DO) and the moisture content of sediment (*Table 1*). However, the concentrations of TOC, Al, Mn, Fe, and Si show significant differences when comparing the values obtained in 2011 and 2013 (p > 0.05). For instance, the average value of TOC, Al, Mn, Fe, and Si was 1.11%, 9.86%, 0.104%, 5.09%, and 22.27%, respectively. In 2013, the average content of the above parameters reached 1.05%, 10.17%, 0.104%, 5.07% and 22.84%, respectively. The dissolved oxygen concentration was 2.88 ~4.72 mg/L in 2011 and 3.94~6.74 mg/L in 2013, indicating that the sampling point was an anoxic area.

The mean concentration of each metal in 2013 was lower than that in 2011 (*Fig.* 2). In 2011, the concentrations of Cd, Cr, Cu, Ni, Pb and Zn were in the ranges of 0.071– 0.150, 27–35, 26–45, 31–204, 6–83 and 138–177 μ g/g, with the averages of 0.108, 31, 32, 90, 76 and 156 μ g/g. In 2013, the respective ranges were 0.057–0.110, 21–30, 23– 35, 26–136, 51–64 and 116–196 μ g/g, with the averages of 0.082, 26, 28, 55, 56 and 121 μ g/g. The average values of Cu, Ni, Pb and Zn were higher than their background values, and close to their background for Cd and Cr. Heavy metal concentrations here generally exceeded the results from earlier studies (Qiao et al., 2010; Xia et al., 2016). There was a big difference on the distribution of Cd and Ni at those sampling sties. According to *Figure 2A* and *C*, Cd was mainly distributed close to the land area (S1, S2, S5, S7 and S11), and Ni near the cage mariculture areas (S2, S4, S5, S8 and S10).

The speciation distribution of heavy metals in the mariculture sediment is shown in *Figure 3*. Cr fractions were not investigated because the valence state is more important than that its bound fraction. Cd mainly was found in F1 33.6 - 63.8% in 2011 and 47.4 - 63.6\% in 2013 and F4 16.9 - 43.4\% in 2011 and 21.9 - 34.8\% in 2013. The dominant

phase of Cu was in F5 53.6~69.2% in 2011 and 51.4~69.0% in 2013 and F4 20.0~32.7% in 2011 and 18.9~29.1% in 2013. Additionally, 5.3~12.2% in 2011 and 6.4~14.4% in 2013 of total Cu concentration existed in F3. The dominant proportion 64.0~74.1% in 2011 and 58.7~67.4% in 2011 of Pb was found in F5, and the proportions of other fractions were in the following order: F4 (12.8~19.5%, 2011), (17.1~26.7%, 2013); F1 (5.8~15.8%, 2011), (7.2~17.4%, 2013). The dominant phase of Zn was in F5, which accounted for 59.0~67.2% in 2011 and 53.0~69.6% in 2013. Ni was mostly retained in F5, representing 61.6~77.6% (in 2011), 58.6~72.5% (in 2013) of total concentration, and then F4 accounted for 8.9~23.6% (in 2011), 13.2~18.3% (in 2013) of total concentration. To sum up, Cu, Ni, Pb, Zn from the sediment were mainly present in the residual fractions, followed by the sulfide bound fractions, and then the content of organic matter bound fractions in Cu was higher than that of Cd, Pb, Ni, Zn. The Cd in the sediments was dominated by sulfide and weak acid fractions, followed by the residual fractions. On the whole, the reducing fractions of five heavy metals were low.

Assessment of the metal contamination

Figure 4 shows the CF values of each heavy metal in 2011 and 2013. It was shown that most of the CF values of the heavy metals in 2013 were lower than that in 2011, and the concentrations of heavy metals varied significantly at the eleven sampling sites. According to the CF values of heavy metals, all sites for Cd were in low degree in both years. The most sites for Cr in 2013 were in low degree, but in moderate degree in 2011. All sites for Cu and Pb were in moderate degree. Zn (at S6 in 2011 and at S8 in 2013) were in considerable degree. Half of the sites for Ni (mainly near the cage mariculture areas) were in very high degree, and heavy metal in this figure were arranged by their pollution degrees, Cd < Cr < Cu < Pb < Zn < Ni. The pollution degrees assessed by CF were higher for Zn, Cu, Cd, Pb, Ni than that by EF and Igeo in our previous studies (Wang et al., 2016.), furthermore, there were unpolluted at all sites for Cr by EF and Igeo. In general, based on CF, EF and Igeo, Cd at all sampling sites was unpolluted, and other heavy metals (except Cr) at all sampling sites were polluted, especially Ni near the cage mariculture areas was polluted in high degree. The PLI values of each sampling site are shown in Figure 5. It was shown that the PLI values in 2013 were lower than that in 2011 at all sites (except S8). At S8, the CF values of Cd, Cu, Zn and Ni in 2013 were higher than that in 2011. In both of 2011 and 2013, the PLI values were over 1.0 at all sites, which indicated that this area was polluted. In this case, despite the comprehensive pollution decreases, heavy metal pollution (especially Cd, Cu, Zn and Ni) at some site of this area should be considered for mariculture actions.

Assessment of risk

Assessment of ecological risk

The weak acid soluble fraction (F1) of Cd, Cu, Pb, Zn and Ni was analyzed, and the spatial distribution of calculated RAC values for those five metals in both two years was shown in *Figure 6* by ArcGIS. The order of ecological risk assessed by RAC was: Cd > Ni > Pb > Cu > Zn. The risk for heavy metals in 2013 was higher than that in 2011 (except Cu), the inconsistency of ecological risk and contamination shown that ecological hazardous risk was heavily affected by bound fractions of heavy metals than by their total concentrations.

The range of RAC values for Cd was from 33.6% to 68.7%, which indicated high to very high risk. In 2011, very high risks for Cd were found at more than 50% of sites, especially at S5 and S9, where RAC values exceeded 60%. In 2013, very high risks for Cd were found in most of the sites (especially at S3 and S8) except S7. The range of RAC values for Ni and Pb was from 5.0% to 17.8%, from 5.80% to 17.4% respectively, which showed low to medium risk. For Ni, the medium risks existed in more than half site in 2011 and more than 70% sites in 2013, and a higher risk was found on S7 and S9 in 2011 and on S4 and S11 in 2013. For Pb, medium risks were contributed from less than half sites in both two years, and it presented higher risk at the S6 and S11 than other sites in 2011, S7 and S10 sites were higher in 2013. The range of RAC values for Cu and Zn were from 1.80% to 5.60%, from 1.80% to 6.30% respectively, which indicated low risk. For Cu, S9 and S10 showed higher risk than other sites in 2011, and S6 and S9 were higher in 2013. For Zn, S1 and S2 showed higher risk than other sites in 2011, and S1 and S10 were higher in 2013.

The order by Hakanson risk index was: Cd > Pb > Ni > Cu > Zn (Wang et al., 2016). The orders by both RAC and Hakanson risk index were approximately the same. However, assessed by Hakanson risk index, the risk degrees was a little lower than that by RAC, the higher risk occurred in 2011. Furthermore, the spatial distribution of ecological risk for each metal was different in two assessment methods.

Assessment of biotoxicity risk

The AVS and SEM concentrations of heavy metals in mariculture sediments were showed in *Table 2*. The AVS concentrations varied with sites, ranging from 0.005 to 2.012 μ mol/g in 2011 and from 0.210 to 1.706 μ mol/g in 2013. The average concentrations of Cd, Cu, Ni, Pb and Zn were 0.0002, 0.187, 0.861, 0.150, 0.898 μ mol/g in 2011, and 0.0003, 0.166, 0.602, 0.130, 0.992 μ mol/g in 2013 respectively. The sums of AVS-SEM, Σ SEM (SEM-Cd + SEM-Cu + SEM-Ni + SEM-Pb + SEM-Zn) at S2 and S8 in 2011 and at S2 and S5 in 2013 were higher than that on the other sampling sites.



Figure 2. The total concentration distribution of each metal at sediment sampling sites in Zhelin Bay



Figure 3. The speciation distribution of each metal at sediment sampling sites in Zhelin Bay

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Figure 4. The CF values of each heavy metal



Figure 5. The PLI values of each sampling site

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Figure 6. The ecological hazardous risk of heavy metals from Zhelin bay

Table 1. Characterization of sediment (n = 6) and water (n = 2) in sampling sites of the Zhelin Bay

	Sediment													Water			
Site	TOC (%)		SMC (%)		Al (%)		Mn (%)		Fe (%)		Si (%)		pH		DO (mg/l)		
	2011	2013	2011	2013	2011	2013	2011	2013	2011	2013	2011	2013	2011	2013	2011	2013	
S 1	1.15	1.14	46.1	49.3	9.64	10.42	0.109	0.135	5.00	5.21	22.4	22.6	8.20	7.33	2.88	4.07	
S2	1.04	1.10	50.0	51.3	10.27	9.98	0.102	0.098	5.26	5.18	22.6	22.1	8.36	7.49	3.81	4.01	
S 3	1.19	0.92	47.9	48.6	10.60	10.73	0.079	0.079	5.16	4.98	22.1	22.9	8.62	7.51	3.97	4.02	
S 4	0.94	0.96	45.5	46.6	10.14	10.72	0.106	0.117	5.29	5.24	21.8	23.7	8.66	7.64	4.19	3.94	
S 5	1.12	1.21	43.5	47.9	9.54	10.30	0.117	0.117	5.16	5.24	21.5	23.5	8.70	7.77	4.72	4.92	
S 6	1.13	0.84	51.6	54.0	9.98	10.13	0.106	0.109	5.24	5.16	22.3	22.1	8.30	7.85	3.60	5.53	
S 7	1.10	0.78	48.6	50.6	10.23	9.68	0.087	0.090	5.18	4.56	22.7	22.4	8.70	7.86	4.10	6.74	
S 8	1.11	0.93	44.6	47.9	9.75	9.99	0.113	0.098	5.13	5.08	22.6	21.8	8.23	7.65	3.66	4.60	
S 9	1.15	1.19	47.0	51.6	9.58	10.24	0.117	0.121	5.00	5.18	21.5	23.2	8.78	7.74	3.45	4.66	
S10	1.12	1.34	48.3	50.1	9.26	9.93	0.087	0.087	4.59	5.03	23.1	23.5	8.02	7.90	3.61	4.91	
S11	1.12	1.10	52.7	53.0	9.52	9.75	0.125	0.098	5.03	4.90	22.4	23.4	8.30	7.80	3.60	5.83	
Avg	1.11	1.05	47.80	50.08	9.86	10.17	0.10	0.10	5.09	5.07	22.27	22.84	8.44	7.69	3.78	4.84	
p	0.288		0.288 0.000		0.043		0.983		0.7	60	0.089		0.000		0.004		

AVS = acid volatile sulfides; TOC = total organic carbon; SMC = sediment moisture contents; Avg: average

The data were statistical mean in the table; p < 0.05: paired t-test revealed that this difference was no significant

Sites	AVS		SEM-Cd		SEM-Cu		SEM-Ni		SEM-Pb		SEM-Zn		∑SEM	
	2011	2013	2011	2013	2011	2013	2011	2013	2011	2013	2011	2013	2011	2013
S 1	0.212	1.053	0.0004	0.0004	0.212	0.227	0.415	0.469	0.132	0.121	0.747	0.781	1.506	1.598
S 2	0.511	0.991	0.0003	0.0006	0.141	0.222	1.969	1.325	0.109	0.199	0.668	1.918	2.887	3.665
S 3	0.797	0.234	0.0002	0.0002	0.129	0.116	1.558	0.315	0.099	0.075	0.742	0.645	2.528	1.151
S 4	0.193	0.128	0.0002	0.0002	0.113	0.139	1.681	0.467	0.108	0.097	0.834	0.733	2.736	1.436
S5	2.012	1.216	0.0002	0.0002	0.329	0.235	0.36	1.227	0.265	0.253	1.033	1.556	1.987	3.271
S 6	0.007	0.359	0.0002	0.0002	0.101	0.137	0.281	0.218	0.083	0.072	0.797	0.747	1.262	1.174
S 7	0.608	1.111	0.0003	0.0001	0.120	0.101	0.306	0.271	0.095	0.067	0.817	0.746	1.338	1.185
S 8	1.637	0.538	0.0002	0.0002	0.316	0.141	0.537	1.172	0.304	0.098	1.752	0.684	2.909	2.095
S 9	1.181	0.210	0.0001	0.0002	0.339	0.208	0.43	0.315	0.261	0.212	1.088	0.839	2.118	1.574
S10	0.525	1.706	0.0003	0.0002	0.142	0.186	1.514	0.437	0.103	0.148	0.713	1.783	2.472	2.554
S11	0.005	0.234	0.0002	0.0002	0.113	0.112	0.418	0.404	0.084	0.082	0.687	0.482	1.302	1.080

Table 2. AVS and SEM concentrations of heavy metals in mariculture sediments in sampling sites of the Zhelin Bay (umol/g)

 \sum SEM = SEM-Cd + SEM-Cu + SEM-Ni + SEM-Pb + SEM-Zn; foc = organic carbon fraction

The ratios of $(\sum \text{SEM-AVS})/f_{OC}$ obtained in our study sites were calculated to 113, 228, 145, 271, -2, 111, 66, 115, 81, 174, 116 µmol/gOC in 2011, and 48, 243, 100, 136, 170, 97, 10, 167, 115, 63, 77 µmol/g OC in 2013, respectively (*Fig. 7*). The results indicated that there were no adverse effects, except S2, S4, and S10 in 2011, and except S2, S5 and S8 in 2013.



Figure 7. The ratios of $(\sum SEM-AVS)/fOC$

The results of no adverse effects by AVS-SEM were in accord with the prediction results by the mean ERL quotients (Wang et al., 2016), which indicated that the ratios of $(\sum \text{SEM-AVS})/f_{OC}$ could accurately be used to judge if there were no adverse effects and be of great help for environmental protection. Then, the uncertain risk part by AVS-SEM model could be compensated by other methods and would be discussed in the next step.

Statistical analysis

The average values of metal elements, characterization parameters and risk assessment values from 2011 to 2013 were analyzed by factor analysis and correlation

analysis. *Figure 8A* was factor loading plot to describe 20 features (six metals, seven characterization parameters and seven risk assessment indexes) from the different sampling sites. *Figure 8B* was factor loading plot for the different sampling sites, each of which was described by 20 features. The correlation analysis was mainly carried out by 15 features (seven risk assessment indexes, six metals, and two characterization parameters), and the results were showed in *Table 3*.



Figure 8. The principal component analysis diagram for heavy metals and different sampling sites

	Igeo	ef	PLI	RAC	ER	SQGs	AVS- SEM	Cd	Cr	Cu	Ni	Pb	Zn	Fe	Si
Igeo	1	0.910**	0.998**	-0.394	0.923**	0.856**	0.519^{*}	0.455^{*}	0.249	0.687^*	0.733^{*}	0.734*	0.567^{*}	0.598^*	-0.355
ef		1	0.920^{**}	-0.523*	0.958^{**}	0.976^{**}	0.750^{*}	0.265	0.180	0.396	0.933**	0.516^{*}	0.465^{*}	0.524^*	-0.229
PLI			1	-0.426	0.936**	0.871^{**}	0.537^{*}	0.454^{*}	0.221	0.675^{*}	0.752^{*}	0.733^{*}	0.548^*	0.590^{*}	-0.355
RAC				1	-0.487^{*}	-0.505	-0.502^{*}	-0.329	0.392	-0.143	-0.52*	-0.035	0.020	-0.067	-0.350
ER					1	0.973**	0.731^{*}	0.224	0.144	0.418	0.902^{**}	0.672^{*}	0.445	0.649^{*}	-0.361
SQGs						1	0.820^{**}	0.133	0.139	0.269	0.975^{**}	0.501^*	0.390	0.582^{*}	-0.259
AVS- SEM							1	-0.298	0.266	-0.057	0.856**	0.244	0.336	0.545*	-0.052
Cd					ĺ			1	-0.397	0.662^{*}	0.048	0.241	-0.135	-0.193	0.090
Cr									1	0.314	0.047	0.360	0.819^{**}	0.454	-0.383
Cu										1	0.078	0.703^{*}	0.486^{*}	0.209	-0.214
Ni											1	0.314	0.253	0.482^{*}	-0.147
Pb												1	0.571^{*}	0.645^{*}	-0.665*
Zn													1	0.586^{*}	-0.521*
Fe														1	-0.613*
Si															1

Table 3. Correlation between the risk assessment indexes and the elements in the sediment of Zhelin Bay

The determinant of coefficient is 0.000; *Correlation is significant at the level of p < 0.05; **Correlation is significant at the level of p < 0.01

In *Figure 8A*, the first factor described 41.76% of the common variance, and the second factor described 15.44%. Rotation of the factor solution was necessary for better interpretation. The first factor was closely linked to Cu, Pb, As in Igeo, and the second factor was closely linked to Ni in AVS-SEM, SQGs, ER. These results indicated that 1) the ecological impacts of Ni were different from the impacts of Cu, Pb, As; 2) Cu and

Pb were the major pollutants in the sediments; and 3) Ni was the main toxicity factor for ecological risk. From the correlation analysis, we concluded that: 1) the pollution factors (I_{geo} and PLI) were significantly and positively correlated with Fe and all heavy metals except Cr; 2) Ni was very significantly and positively correlated with SQGs, Hakanson risk index and AVS-SEM, followed by Fe; 3) Pb was significantly and positively correlated with SQGs and Hakanson risk index; 4) Si was negatively correlated with most of the heavy metals, which showed that the metal pollutants were mostly from human activities.

The factor scores were used to analyze the contamination sources. In *Figure 8B*, the first factor for the common variance was 96.39% with high contribution from S1 and S7. The second described 2.70% and highly loaded by S2 and S4. Near to Sanbai Men port that was occupied in fishery and trade, the locations of the four sites were concentrated in the northwest coastal area of the semi-closed bay. It is evident that the wasters from the fishery, trade, port construction and other urban activities resulted in the serious environmental pollution. On the other hand, in the cage area for the fish and maricultrure, vessel activities were frequent, which suggested that the primary pollution sources were from the combustion of gasoline and diesel fuel (Zhu et al., 2016; Yuan et al., 2015).

Conclusions

In this study area, all the sampling sites were polluted by heavy metals (Zn, Cu, Cr, Pb, Ni). The concentrations of heavy metals in 2013 were lower than that of 2011, and the residual fraction and sulfide bound fraction were the primary fractions of heavy metals. For each metal, Ni posed a moderate to very high risk; Zn and As posed a moderate to considerable risk; Cr, Cu and Pb were at a moderate degree; Cd was unpolluted at the sampling sites. From the aspects of ecological risk, a medium to very high risk came from Cd, Ni and Pb. Except for the cage mariculture area (S2, S5 and S8), all the sites would be expected no biotoxicity. Through analyzing the various factors about the heavy metals, four sites (S1, S2, S4 and S7) were profoundly affected by the environmental pollutants which primarily resulted from the combustion of gasoline and diesel fuel and the ship protective layer. The intensive mariculture activity is one of the main reasons for the heavy metal pollution and ecological risk of sediments in Zhalin bay. The exploration of effective strategies is quite necessary in the future for keeping a good quality of the coastal environment and sustainable mariculture development.

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