

## **Distribution, Speciation and Ecological Risk Assessment of Heavy Metals in the Surface Sediments of Sanmen Bay in ZheJiang**

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**Abstract.** This Surface sediment samples were collected from Sanmen Bay in Zhejiang. The distribution of total concentration of five heavy metals (Zinc, Chromium, Cadmium, Copper, and Lead) was determined, and their speciation using BCR sequential extraction procedure was investigated. The pollution level and ecological hazard of these heavy metals were evaluated Potential Ecological Risk Index ( $E_r^i$ ). The distribution of five metals showed that the total concentrations in inner bay were higher than those in out of bay. The results of metal speciation in surface sediment show that the residual fraction of four metal except for Pb predominated, of which Zn account for 79.20%~84.25%, Cr 93.24%~96.16%, Cd 34.71%~57.58%, and Cu 66.06%~79.51%, respectively. The dominate fraction of Pb is the part bounded to amorphous Fe and Mn oxides and hydroxides, which accounts for 58.17%~72.7%. The evaluation results indicate that Cd is the primary element with slight ecological risk in the area according to the potential ecological risk index ( $E_r^i$ ).

### **Introduction**

The heavy metals which were discharged into sea could be transferred between sea water and marine sediments by means of the effects such as adsorption/desorption, diagenesis, and biological pumps[1]. Heavy metals are commonly toxic, which bring negative effects toward aquatic organisms after biouptake. These toxicants may accumulate in food chains and present threats to human health finally[2]. The researches about the ecotoxicity of heavy metals always distract global attentions [3-6]. The surface sediments play a important role in the transfers of heavy metals as a main part of circulation of substance in marine environments[7]. Though the total amount of heavy metals indicates the pollution level, it cannot reflect the potential risks [8]. The capability of biouptake and transfer of heavy metals were determined by their speciation, which hence affect their environment potential risks[9].

Sanmen bay is located in the east of Zhejiang province of China, and it makes a great contribution to the local economy. With the rapid development of industry such as thermal power generation, nuclear power, reclamation projects, and shipbuilding in the area near Sanmen bay, the environmental quality has been significantly affected[10]. Slight pollution of copper and chromium was reported in eutrophic area of sanmen bay[11,12]. The researches on the seawater, marine sediments, and shell creatures in sanmen bay reveal that the sediments has been contaminated by copper[13,14]. The discharges of the domestic sewage and industrial waste water have become the main source of pollution, in which heavy metals predominated. It is necessary to investigate the source, transfer, and pollution level of heavy metals in sanmen bay.

With the surface sediments of sanmen bay, five heavy metals (Zinc, Chromium, Cadmium, Copper, and Lead) was determined, and their speciation using BCR extraction method was investigated in this work. The pollution level and ecological hazard of these heavy metals were evaluated with Potential

Ecological Risk Index ( $E_r^i$ ). The results will help to evaluate the current environmental quality of sanmen bay.

## Materials and Methods

### Study areas

The study was performed in Sanmen Bay in January 2016 (Fig. 1). The stations can be divided into two categories. 15 stations were located inside the Bay, where was near to areas with high density of population (Fig. 1) while the other 6 stations were located outside the Bay.

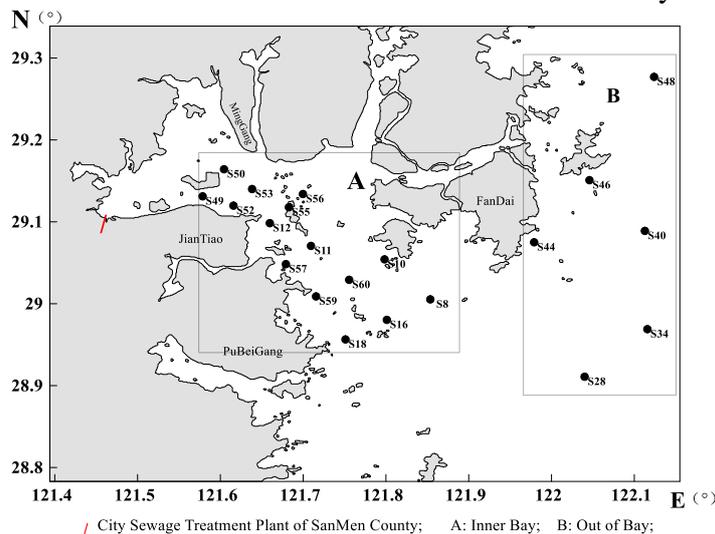


Fig. 1 Location of sampling sites

### Sediment collection strategy

Sediment samples were collected using a box-corer. Surface sediments (1~2 cm) were carefully collected into a polyethylene bag using a hand-trowel, and stored frozen ( $-20\text{ }^{\circ}\text{C}$ ). Frozen samples were firstly freeze-dried with a freezer (DELTA1-24 LSC, Germany). After that, they were grinded with an agate mortar, filtered with 250 mesh nylon sieve, and finally were stored in clean polyethylene bags in a dryer.

### Analysis method

An improved BCR (Measurements and Testing Programme) three-step sequential extraction procedure was used for extraction of heavy metals with different species [15]. In this method, the extracted heavy metal can be classified into 3 categories: soluble and exchangeable (F1), bound to Fe-Mn oxide (F2), bound to organic matter and sulfides (F3), and residual (F4). The extraction was conducted according to the following steps:

$0.800\pm 0.002$  g of surface sediment was placed in a polypropylene centrifuge tube with a plug. All experiments were carried out in duplicate.

F1 (step1). Add 32 ml of 0.1 mol/L HAc in a centrifuge tube, then stopper and extract by shaking for 16 h at  $22\pm 5\text{ }^{\circ}\text{C}$ . Separate the extract from the solid residue centrifugation at 3000 r/min for 20 min and decant the supernatant liquid into a polyethylene container. Add 1 mL concentrated  $\text{HNO}_3$  immediately, store the samples in a refrigerator at about  $4\text{ }^{\circ}\text{C}$  prior to analysis. Wash the residue by adding 15 mL of distilled water, shaking for 15 min on the end-over-end shaker and centrifuging for 20 min at 3000 r/min. Decant the supernatant and discard, taking care not to discard any of the solid residues. The extraction was repeated twice.

F2 (step 2). Add 32 mL of freshly prepared  $\text{NH}_2\text{OH}\cdot\text{HCl}$  solution (0.5 mol/L) to the residue from step 1 in the centrifuge tube. Resuspend by manual shaking, stopper and then extract according to step 1.

F3 (step 3). Carefully add 8 mL of 30%  $\text{H}_2\text{O}_2$  solution (acid-stabilised to pH 2~3) to the residue in the centrifuge tube in small aliquots to avoid losses. Cover the vessel loosely with its cap and digest at room temperature for 1 h. Continue the digestion for 1 h at  $85\pm 2\text{ }^{\circ}\text{C}$  in a water bath, then reduce the volume to less than 2 mL by further heating of the uncovered tube. Add a further aliquot of 8 mL

30% H<sub>2</sub>O<sub>2</sub> solution. Heat the covered vessel again to 85±2 °C and digest for 1 h. Add 32 mL of 1 mol/L NH<sub>4</sub>OAc solution (acid-stabilised to pH 2.0±0.1) to the cool moist residue and shake for 16 h at 22±5 °C. Separate the extract from the solid residue by centrifugation and decantation as in step 1. Stopper and retain as before for analysis.

F4 (step 4). The residue from steps 3 was dried to constant weight at 60 °C. 6 mL concentrated HNO<sub>3</sub>, 2 mL concentrated HCl and 2 mL HF were added to 0.20 g of the dried residue. Digest by microwave, drive the added acid and constant volume to 50 mL.

All reagents used in the extraction processes were GR grade. The contents of heavy metals were determined by atomic absorption spectrometric method (ZEEnit700P, Jena, Germany). The pretreatment process of samples were carried according to 'People's republic of China Marine Industry Standard' (HY/T 132 2010).

The content of total organic carbon (TOC) in surface sediment was determined by Element Analyzer (Elementary Vario MICRO cube) and the sediment particle size was measured by Laser Particle Size Analyzer (Master Sizer3000, UK).

The data was analyzed with the software of Origin 9.0 and SPSS 18.0.

#### Quality control

The quality control of sequential extraction was conducted using the national standard material GBW 07314 (Second Institute of Oceanography, State Oceanic Administration). Different fractions were used to test the accuracy of sequential extraction [16, 17].

$$R (\%) = [(C_{F1} + C_{F2} + C_{F3} + C_{F4}) / C_{Total}] \times 100\% \quad (1)$$

Where C<sub>F1</sub>, C<sub>F2</sub>, C<sub>F3</sub> and C<sub>F4</sub> present fraction of different states, C<sub>Total</sub> present the total quality obtained by direct determination, and R present the ratio of the rate of recovery.

The results showed that the recovery rates of 5 heavy metals ranged from 80.4% to 116.6%. The total recovery rates of these 5 heavy metals ranged from 91.4% to 102.06%. And the recovery rate of TOC varied from 91.7% to 103.47%. The relative deviation was lower than 10%, showing the results were reliable.

#### Potential ecological risk [18]

For single heavy metal

$$C_f^i = C^i / C_n^i \quad (2)$$

Where C<sub>f</sub><sup>i</sup> is the single element pollution factor, C<sup>i</sup> is the content of the i element in samples and C<sub>n</sub><sup>i</sup> is the reference value of the i element.

For an area

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

Where E<sub>r</sub><sup>i</sup> is the potential ecological risk index of an individual i element. T<sub>r</sub><sup>i</sup> is the biological toxic factor of an individual i element.

The potential ecological risk of sediment with several species of heavy metal is the sum of E<sub>r</sub><sup>i</sup>.

$$RI = \sum_i^m E_r^i = \sum_i^m T_r^i \cdot C_f^i = \sum_i^m T_r^i \cdot C^i / C_n^i \quad (4)$$

## Results and discussion

### Geochemical properties of the surface sediments

As is shown in Fig. 2f, the particle size is small, and silt is the main type with proportion up to 70.04%. Clay followed with the proportion of 26.82%. The percentage of organic matter in sediment is between 0.34% to 0.67%, with the average of 0.52%. According to the environmental sediment criteria of China (GB 18668-2002), the surface sediment in sanmen bay can be classified as grade 1.

### 3.2 Distribution of heavy metals in the surface sediments

The amount of Zn in the surface sediment ranged in 71.30mg/kg and 114.12mg/kg, with the average of 97.67mg/kg. The amount of Cd ranged in 0.10mg/kg and 0.15mg/kg, with the average of 0.13mg/kg. The amount of Cr ranged in 63.59mg/kg and 102.25mg/kg, with the average of

88.69mg/kg. The amount of Cu ranged in 25.76mg/kg and 43.40mg/kg, with the average of 34.45mg/kg. The amount of Pb ranged in 12.75mg/kg and 28.48mg/kg, with the average of 22.29mg/kg. As is shown in Fig. 2a to 2e, the spatial distributions of Zn, Cd, Pb, Cr, and Cu were basically the same, which all show the tendency of higher metal concentrations in inner bay. The research area is almost surrounded by land, and also near to residential living area. The high concentration of heavy metals probably attributes to human activities in this area. Moreover, there was a small area with high metal concentrations in station S49. The upstream sewage plant discharge may be its main source.

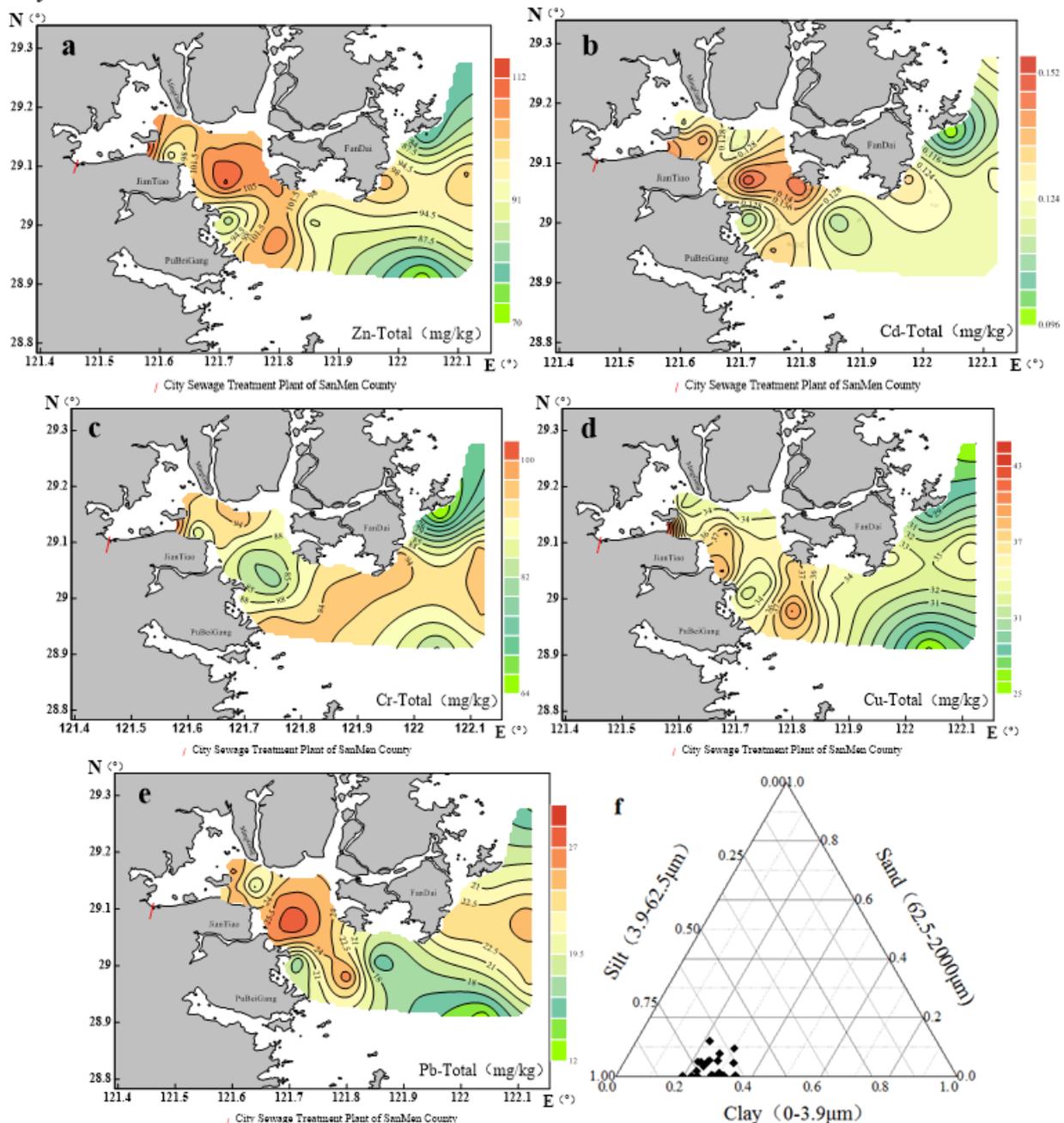


Fig. 2 The distribution of total concentration and granulometry of heavy metals

According to the correlation analysis among heavy metal amount and characteristic parameters, the information about the source and controlling factors in their transfer can be obtained[19]. The correlation analysis were done in total amount of heavy metals, particle size, and organic matter, and related marix could be seen in Table 1.

**Table 1** Correlation matrix of geochemical characters of sediment and heavy metal contents

	Silt	Clay	Organic matter	Zn	Cd	Cr	Cu	Pb
Silt	1							
Clay	-0.731**	1						
Organic matter	-0.468*	0.431	1					
Zn	-0.648**	0.684**	0.527*	1				
Cd	-0.427	0.512*	0.257	0.631**	1			
Cr	-0.424	0.336	0.356	0.676**	0.353	1		
Cu	-0.505*	0.550**	0.419	0.872**	0.523*	0.633**	1	
Pb	-0.612**	0.541*	0.642**	0.781**	0.375	0.281	0.620**	1

(1)\*means significantly correlated in 0.05 level; (2)\*\* means significantly correlated in 0.01 level

Zn, Cu, Cd, and Pb both correlated with clay to a certain degree. Zn and Cu significantly correlated with clay ( $p < 0.01$ ), which means that clay is one of main reason controlling the spatial distribution of zinc and copper. Pb significantly correlated with organic matter ( $p < 0.01$ ), which means that organic matter is one of main reason controlling the spatial distribution of lead. The good relationships between five heavy metals, except for Cd-Cr, Cd-Pb, and Cr-Pb, indicates a same source for them. The poor correlations for Cd-Cr and Cd-Pb partly attributed to the good mobility of Cd and another to the source of Pb. Lead may comes from land or wet or dry depositin from atmosphere, whcih may also explain the poor correlationship of Pb and Cr[20].

### 3.3 Speciation of heavy metals in the surface sediments

Four fractions for each metal (F1: exchangeable, F2: reducible, F3: oxidable, F4: residual) after extraction were obtained with BCR sequential extraction procedure [21, 22]. The fractions from F1 to F3 were defined as extractable state, which was considered to have potential risk for environment [23].

Fig. 3 shows the distributions of four fractions in five heavy metals. It is shown that Zn has the highest total amount with the majority in F4 (79.20% to 84.25%). The proportion of F2 for Zn was from 9.66% to 13.23%. The proportion of F1 and F3 were relatively low with the range of 3.24% to 4.79% and 2.35% to 3.73%, respectively. Low proportion of F1 attributed to the capability of Zn to be easily adsorbed and assimilated by other organisms [24]. Similar to Zn, the majority of Cr was in F4 (93.24% to 96.16%), followed with F3 1.69% to 3.12%, F2 1.25% to 2.0%, and F1 0.11% to 0.16%, respectively. Poor mobility of Cr was found in sediment of research area. The F4 fraction of Cd accounts for 34.71% to 57.58% with a lower F1 from 25.14% to 37.76%. The substance of  $Cd_{\alpha}Ca_{1-\alpha}CO_3$  could be formed for Cd with carbonates and calcareous minerals [25]. High proportion of Cd leads to an easy way of going back to water. The F2 fraction of Cd accounts for 5.86% to 22.44%. The high proportions of F1 and F2 of Cd indicate its good transferability and ecotoxicity. The speciation of Cu was similar to Zn. The majority of Cu was in F4 (66.06% to 79.51%), followed with F2 17.66% to 28.09%, F1 1.96% to 4.69%, and F3 0.84%~1.30%, respectively. However, Pb was different with others. The majority of Pb was in F2 3.39% to 69.02%, followed with F4 27.3% to 41.83%, F1 1.05%~4.44%, and F3 2.14%~2.98%, respectively. It means that Pb has high potential risk but poor transferability.

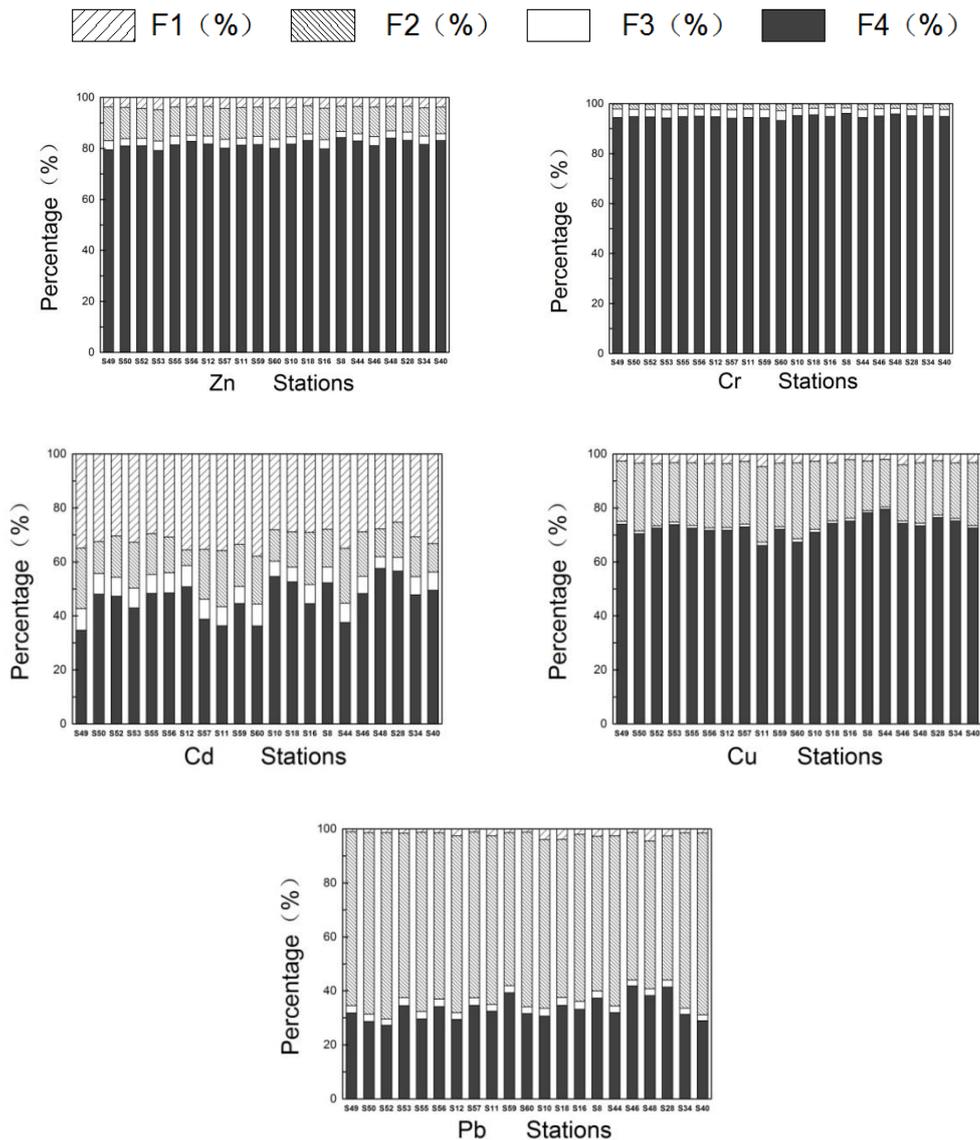


Fig.3 The distribution of fractions in heavy metals

Ecological risk assessment of heavy metals

Potential ecological risk index was raised by Hakanson in 1980s, which is an evaluation method for heavy metal pollution based on sedimentation principles[26,27]. The background ( $C_n^i/mg.kg^{-1}$ ) of Zn, Cd, Cr, Cu, and Pb were set as 75, 0.1, 75, 20, and 27, respectively. The  $T_r^i$  were set as 1, 30, 2, 5, 5, respectively according to literatures[18, 28]. Eq.2 to Eq. 4 were used and the results are shown in Table 2,

Table 2 Dividing standards of heavy metals ecological risk levels[18]

$E_r^i$	Ecological risk levels for single toxicant	RI	Total ecological risk levels
$0 < E_r^i < 40$	slight	$RI < 150$	slight
$40 \leq E_r^i < 80$	medium	$150 \leq RI < 300$	medium
$80 \leq E_r^i < 160$	severe	$300 \leq RI < 600$	severe
$160 \leq E_r^i < 320$	very severe	$RI \geq 600$	very sever
$E_r^i \geq 320$	extreme severe		

Generally, the  $E_r^i$  value of inner bay were more than that of our of bay. It means that the pollution level in inner bay is more severe than that of out of bay. The averages of  $E_r^i$  values follow the order of  $Cd > Cu > Pb > Cr > Zn$ . The  $E_r^i$  values of Cu, Pb, Cr, and Zn are less than 40, and mean slight ecological risk. Medium ecological risk were found in the stations of S49, S52, S53, S11, S10, and S18. The locations indicates human activities are probably the main source of Cd. The whole area is at slight ecological risk level according to RI.

## Conclusions

The spatial distributions for five heavy metals are basically same, which indicates a same source. The concentration of heavy metals in inner bay are higher than that of out of bay show us the impacts from human activities. The evaluation results indicate that Cd is the primary element with slight ecological risk in the area according to the potential ecological risk index ( $E_r^i$ ).

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