

Article

Heavy Metal Distribution in Surface Sediments of the Coastal Pearl Bay, South China Sea

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Abstract: Six heavy metals (As, Cu, Cd, Zn, Cr, and Pb) in surface sediments (0–5 cm) from the twenty selected sites of the coastal Pearl Bay (South China Sea) were analyzed to assess the distribution pattern and potential ecological risk. Overall concentrations (mg/kg, dw) in the sediment samples were: As (10.88 ± 6.50), Cu (24.16 ± 18.63), Cd (0.55 ± 0.78), Zn (48.53 ± 30.06), Cr (35.78 ± 28.66), Pb (31.28 ± 18.50). Results showed that the overall mean values of Cd concentrations exceeded the standard of China Marine Sediment Quality, caused by significantly high levels of Cd contents in five sites (S8, S11, S13, S16, and S17) at the offshore area of Pearl Bay. Generally, the metal concentrations showed a decreasing trend from the offshore area to the inner bay. Various index values such as the geo-accumulation index (I_{geo}), the ecological risk index (E_{ri}), and the contamination factor (CF) demonstrated that the coastal Pearl Bay was not polluted by the examined metals except for Cd, which might cause contamination and ecological risk in the region. Principal component analysis (PCA) results indicated that Cu, Zn, and Cr might originate from natural sources inland, and Pb and As might come from the gasoline and diesel fuel from engine boats. It is recommended that further research should focus on detecting the acute source and transferring mechanisms of the toxic metal Cd.

Keywords: heavy metals; surface sediment; ecological risk assessment; Pearl Bay



Citation: Yang, C.; Yu, G.; Liu, Y.; Shan, B.; Wang, L.; Sun, D.; Huang, Y. Heavy Metal Distribution in Surface Sediments of the Coastal Pearl Bay, South China Sea. *Processes* **2022**, *10*, 822. <https://doi.org/10.3390/pr10050822>

Academic Editor: Andrea Petrella

Received: 31 March 2022

Accepted: 20 April 2022

Published: 21 April 2022

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1. Introduction

Heavy metals, especially those so-called non-essential elements such as Cd, Pb, As, and Hg have always been a hotspot of environmental investigations due to their potential to cause severe health risks [1]. Environmental hazard cases such as itai-itai disease and Minamata aroused great social concerns about metal pollution in aquatic systems [2,3]. Nowadays, sediments have been proven to serve as reasonable recorders and indicators for monitoring pollution in aquatic ecosystems such as rivers, lakes, estuaries, oceans, and so on [4–6]. Sediments tend to accumulate varieties of polluting species, such as heavy metals, persistent organic pollutants, and so forth [7,8]. Additionally, those pollutants in sediments may enter the water body under some conditions and thus affect the water quality and may cause some negative effects on the organisms [9]. The metals could be accumulated in the organisms and transferred through food chains. So, the metal pollution in the sediments may pose risks to both the environment and human health [10].

Pearl Bay, a semi-closed bay located in the northern part of the Beibu Gulf, South China Sea, is one of the most important aquaculture bases of pearl oyster and mud crab [11]. It is also a famous tourist attraction known for its lengthy coastline, beautiful beach, and plentiful mangrove resources [12]. The area of this bay is about 168 km^2 , with a large

mangrove area of 1086.25 hm² [11]. Currently, with the development of Fangchenggang City (Guangxi Province, China), anthropogenic factors such as aquaculture, tourism, port construction, and pollutant emissions from the land have posed real threats (for example, eutrophication and inorganic pollution) to the environment of this area [11–13]. Previous studies have reported the metal pollution in both of environmental and biotic matrix of the Beibu Gulf [11–16]. However, specific investigations on the metal pollution issues focusing on this bay are still scarce.

The aim of this work was to study the levels, spatial distribution, and ecological risks of heavy metals in the sediments in the surrounding sea areas of Pearl Bay, South China Sea. Thus, surface sediments samples were collected and measured for trace elements, and some physi-chemical properties of those compartments were analyzed hoping to provide some useful data information for the environmental management and assessment of this bay area.

2. Materials and Methods

2.1. Study Area and Sample Collection

In September 2020, surface sediments sampling was conducted from the surrounding sea area of Pearl Bay using a Peterson grab sampler (Figure 1). For comparison, the study area was divided into four subareas (Area I to Area IV), representing the inner bay area, estuary area, coastal area, and offshore area, respectively. The surface sediments (0–5 cm) were collected using a polyethylene scraper. For each sampling site, five replicate samples were well mixed, and then immediately encapsulated in clean polyethylene packages. Finally, a total of 20 sediment samples were collected from the study area. After collection, the surface sediment samples were clean stored at –20 °C until further analysis.

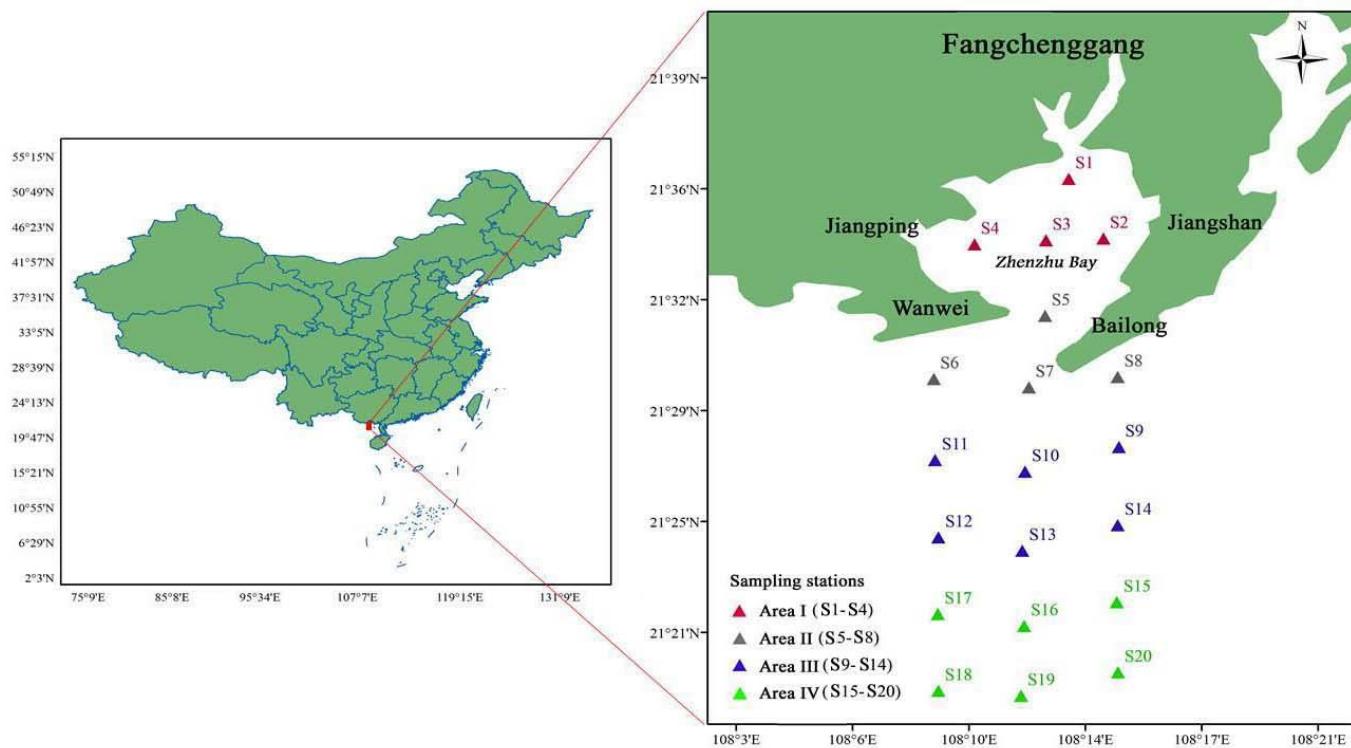


Figure 1. Location of the study area and sampling sites in the coastal Pearl Bay.

2.2. Analysis Method

In the laboratory, sediment samples were frozen-dried, ground, and pass through a 0.5 mm sieve. Approximate 0.15 g sediment samples were transferred into the digestion vessel, adding a mixture of 2 mL nitric acid, 6 mL hydrochloric acid, and 1 mL hydrofluoric

and digested using a high-performance microwave digestion system (Ethos UP, Milestone, Italy) at 190 °C for 30 min. After finishing the procedure, evaporation was then conducted on a hot plate. Then, the digested samples were diluted to a specified volume by adding 5% HNO₃. After filtration, heavy metals were determined for copper (Cu), zinc (Zn), lead (Pb), cadmium (Cd), and chromium (Cr) by using an inductively coupled plasma mass spectrometer (ICP-MS) (PerkinElmer ELAN 9000/DRC-e). Arsenic (As) was analyzed by using the method of Atomic Fluorescence Spectrometry (AFS). Total organic carbon (TOC) values of samples were measured using the potassium dichromate oxidation-ferrous sulfate titrimetry method (GAQS-IQ, 2008) according to Lei et al. (2013) [13]. In the present study, the data of element concentrations were presented in mg/kg dry weight (dw).

In order to maximize the accuracy of the results, several quality control measures were conducted mainly including reagent blank, sample blank, reference materials (ERM-S-510204, China), and duplicate samples were analyzed three times. The standard variations of the elemental analysis of a sample were within the range of 5–10%. The recoveries of reference materials ranged from 72–124%. All glassware and digestion vessels were acid-washed with 10% HNO₃ and rinsed with double distilled water to avoid possible contamination.

In the present study, the Kolmogorov–Smirnov test was used to assess the data normality, and all the data showed normal distribution. Principal component analysis (PCA), hierarchical clustering analysis, and Pearson correlation (PC) analysis were performed to explore associations among heavy metals in the surface sediments and their potential sources. All statistical analyses were conducted using the statistical package SPSS 19.0 (SPSS Inc., Chicago, IL, USA).

2.3. Potential Ecological Risk Assessment

2.3.1. Geo-Accumulation Index

Geo-accumulation indices were calculated based on the following Equation [17]:

$$I_{geo} = \log_2 [C_i/(1.5 \times B_i)] \quad (1)$$

where C_i was the concentration of the element, and B_i was the background value of the element [18]. The factor 1.5 was multiplied to minimize the impact of the lithogenic effect and enrichment caused by sediment inputs from multiple sources. According to the values of the I_{geo} index, the pollution degrees could be divided into seven classes (Table 1).

Table 1. Geo-accumulation index (I_{geo}) and pollution levels for heavy metals.

Class	I_{geo} Value	Pollution Level
0	$I_{geo} \leq 0$	Practically unpolluted
1	$0 < I_{geo} \leq 1$	Unpolluted to moderately polluted
2	$1 < I_{geo} \leq 2$	Moderately polluted
3	$2 < I_{geo} \leq 3$	Moderately to highly polluted
4	$3 < I_{geo} \leq 4$	Highly polluted
5	$4 < I_{geo} \leq 5$	Highly to very highly polluted
6	$I_{geo} > 5$	Very highly polluted

2.3.2. Potential Ecological Risk Index

The potential ecological risk index (RI) has been frequently used to assess the ecological risk degree of heavy metals in aquatic sediments [19]. This method not only assessed the pollution levels in the sediments but also combined ecological and environmental effects with toxicology providing a better evaluation of the potential risks of heavy metal contamination with the index level [9,12].

The contamination factor (CF) was firstly calculated for each sediment sample using the equation [20]:

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

where C_f^i is the contamination factor of the element i in sediment sample; C_s^i is the concentration of element i in the sediment sample; C_n^i is the geochemical background value of element i . Based on the C_f^i values, the contamination degrees could be divided into low contamination (<1), moderate contamination (1–3), considerable contamination (3–6), and very high pollution (>6).

The RI is calculated by the following equations [20]:

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

$$RI = \sum_{i=1}^n E_r^i = \sum_{i=1}^n T_r^i \cdot (C_s^i / C_n^i) \quad (4)$$

where E_r^i is the potential ecological risk factor of the heavy metal i , T_r^i is the toxic response factor of the element i . The T_r^i values for Cd, As, Cu, Pb, Cr, and Zn are 30, 5, 5, 5, 2, and 1, respectively [8]. The classification and interpretation of the values of E_r^i and RI indices were given in Table 2.

Table 2. Indices and corresponding degree of potential ecological risk assessment.

E_r^i	Grade of Ecological Risk of Single Metal	RI	Grade of Ecological Risk of the Environment
$E_r^i < 40$	Low	$RI < 150$	Low
$40 \leq E_r^i < 80$	Moderate	$150 \leq RI \leq 300$	Moderate
$80 \leq E_r^i < 160$	Considerable	$300 \leq RI < 600$	High
$160 \leq E_r^i < 320$	High	$RI \geq 600$	Very high
$E_r^i \geq 320$	Very high		

3. Results and Discussion

3.1. Abundance of Heavy Metals in Sediments

The concentrations of As, Cu, Pb, Cd, Zn, and Cr in sediments from Pearl Bay and the offshore area were shown in Table 3. The ranges of the contents of the six metals are 3.58–28.64, 0.32–67.86, 9.61–68.66, 0.02–2.65, 6.39–110.46 and 4.53–94.51 mg/kg for As, Cu, Pb, Cd, Zn and Cr, respectively, generally showing an order of Zn > Cr > Pb > Cu > As > Cd (by comparing the average values: 48.53, 35.78, 31.28, 24.16, 10.88, 0.55 mg/kg, respectively). This observation was in line with that reported in the Beibu Gulf in 2021 [21] but slightly different from that reported in the eastern Beibu Gulf in 2013 with a Zn > Cu > Cr > Pb > As > Cd sequence [22]. The maximum value of each element seemed to be 1–2 orders higher than the corresponding minimum value, suggesting the heterogeneity of the distribution of metals. The concentrations of the six metals in sediments of coastal Pearl Bay tended to be at a low to medium level compared with those reported from some other bays around the world (Table 4).

When compared with background values of related elements in the sediment of the South China Sea [18], the frequent over-standard phenomenon could be observed, suggesting that anthropogenic activities such as aquaculture have resulted in extra input of heavy metals. Compared with the standard values supposed in the National Standard of China for Marine Sediment Quality (GB 18668-2002), the average concentrations of Zn, Cr, Pb, Cu, and As were all within the range of Grade I (150, 80, 60, 35 and 20 mg/kg for Zn, Cr, Pb, Cu and As, respectively), while the average concentration of Cd was within the range of Grade II, indicating the sediments of Pearl Bay might not suffer from serious pollution of Zn, Cr, Pb, Cu, and As. In China, characteristics of Grade I marine sediment quality can be summarized as without carcasses of large animals and plants, without abnormal color and bad smells, and without submarine industries. It was mentioned that 75% of the samples were found with concentrations of Cd much lower than 0.5. The concentrations of the six metals in the sediments of Pearl Bay tended to be at a low to medium level compared with those reported from some other bays around the world (Table 4).

Table 3. Total organic carbon (TOC, 10^{-3} mg/kg) and heavy metal concentrations (10^{-6} mg/kg) in the surface sediments of the coastal Pearl Bay.

Site	TOC	As	Cu	Pb	Cd	Zn	Cr
S1	8.53	5.31	13.51	10.87	0.12	31.45	13.32
S2	3.03	7.42	7.87	12.42	0.02	24.29	14.14
S3	4.27	7.28	7.91	12.17	0.04	25.84	15.35
S4	5.78	5.25	7.95	12.3	0.45	27.14	16.15
S5	3.21	4.26	44.91	9.61	0.05	18.72	13.87
S6	2.89	9.5	10.18	21.84	0.22	29.7	4.53
S7	3.16	10.46	0.32	11.92	0.27	6.39	22.09
S8	23.66	6.79	13.09	19.56	1.1	29.18	33.48
S9	11.14	7.19	21.13	34.97	0.06	40.27	17.47
S10	18.57	17.94	38.7	49.36	0.08	68.4	60.85
S11	19.4	3.58	10.41	11.04	1.86	15.35	19.71
S12	14.17	10.03	20.36	37.06	0.11	73.94	7.31
S13	14.03	19.56	59.24	55.06	1.33	90.27	44.77
S14	26.55	28.64	67.86	68.66	0.15	110.46	94.51
S15	18.16	15.99	47.11	52.32	0.08	72.33	60.54
S16	29.17	18.03	32.03	50.27	2.65	63.03	79.66
S17	3.03	5.92	12.79	30.86	1.9	35.18	7.46
S18	3.3	6.41	15.25	35.81	0.07	50	46.95
S19	15.27	15.24	24.98	45.22	0.08	104.61	54.9
S20	11.28	12.72	27.67	44.22	0.37	54.04	88.57
Range	2.89–29.17	3.58–28.64	0.32–67.86	9.61–68.66	0.02–2.65	6.39–110.46	4.53–94.51
Mean	11.93	10.88	24.16	31.28	0.55	48.53	35.78
MSQ-1 *	-	20	35	60	0.5	150	80

* MSQ-1 is the Marine Sediment Quality standard criteria (GB 18668-2002) issued by the China State Bureau of Quality and Technical Supervision (CSBTS).

Table 4. Metal concentrations (mg/kg, dw) in sediment samples from this study region and other selected bays around the world.

Locations	Cu	Zn	As	Cd	Pb	Cr	Reference
Pearl Bay, China	0.32–67.86 (24.16)	6.39–110.46 (30.06)	3.58–28.64 (10.88)	0.02–2.65 (0.55)	9.61–68.66 (31.28)	4.53–94.51 (35.78)	the present study
Fangcheng Bay, China	2.7–50.9 (10.9)	15.1–156.0 (41)	2.73–15.89 (6.83)	0.01–0.45 (0.08)	4.9–97.7 (19.2)	n.a.	[13]
Beibu Gulf, China	0.7–73	3.5–161	1.1–19	0.01–0.45	2.4–62	2.1–51	[21]
Fangcheng Bay, China	7.1–34.8 (20.53)	25.4–100.2 (62.37)	3.9–10.8 (7.0)	0.03–0.45 (0.26)	33.2–59 (43.53)	12.2–43.4 (28.5)	[23]
Jiuzhen Bay, China	3.4–5.9	12–29	20–30	0.24–0.50	0.25–0.45	n.a.	[24]
Haizhou Bay, China	3.1–29	6.5–93	2.5–13.7	0.04–0.14	9.3–32	13–79	[25]
Makadi Bay, Egypt	4.1–25	21–121	n.a.	n.a.	13–76	0.01–6.6	[26]
Ha Long Bay, Vietnam	3.8–42	6.3–120	1.8–14	0.03–0.2	10–70	n.a.	[27]
Laucala Bay, Fiji	78–490	16–69	117–234	5.5–9.2	n.a.	n.a.	[28]
Mirs Bay, China	8–42	55–290	5.3–10	n.a.	26–99	20–38	[29]
Bohai Bay, China	28	87.6	11.8	0.25	24.3	72.4	[30]
Laizhou Bay, China	10.99	50.63	7.1	0.19	13.37	32.69	[31]
Liaodong Bay, China	18.90	77.22	10.24	0.34	18.77	n.a.	[32]

Note: n.a. indicates the related data is not available.

3.2. Spatial and Temporal Variation of Heavy Metals

In the present study, contour maps were used to describe the spatial distributions of the heavy metal concentrations in the coastal Pearl Bay (Figure 2). For longitudinal comparison, concentrations of the six metals in the inner bay showed generally lower levels than those in the offshore area, with the high metal content areas concentrated in the southern parts (Area III and Area IV) of the study region. The contents of As, Cu, and Pb exhibited similar distribution patterns, with decreasing values from the southeast to the northwest of the sampling area. Meanwhile, the spatial distributions of Zn and Cr displayed similar patterns, with three concentrated regions appearing in the southeastern area. Cd was an exception, and showed three high concentration zones in the southwest part, suggesting a different source and enrichment mechanism for this metal. Additionally, TOC values were found to be significantly positively correlated with most of the selected metals, except Cd. Similar relationships between TOC and heavy metals were also reported in previous studies nearby the out sea areas of Pearl Bay [27,33], suggesting that the abundance of heavy metals in the sediments may be burdened by organic matters. It is well documented that benthic organisms have a high affinity and play a major role in determining heavy metals in the aquatic environment [22].

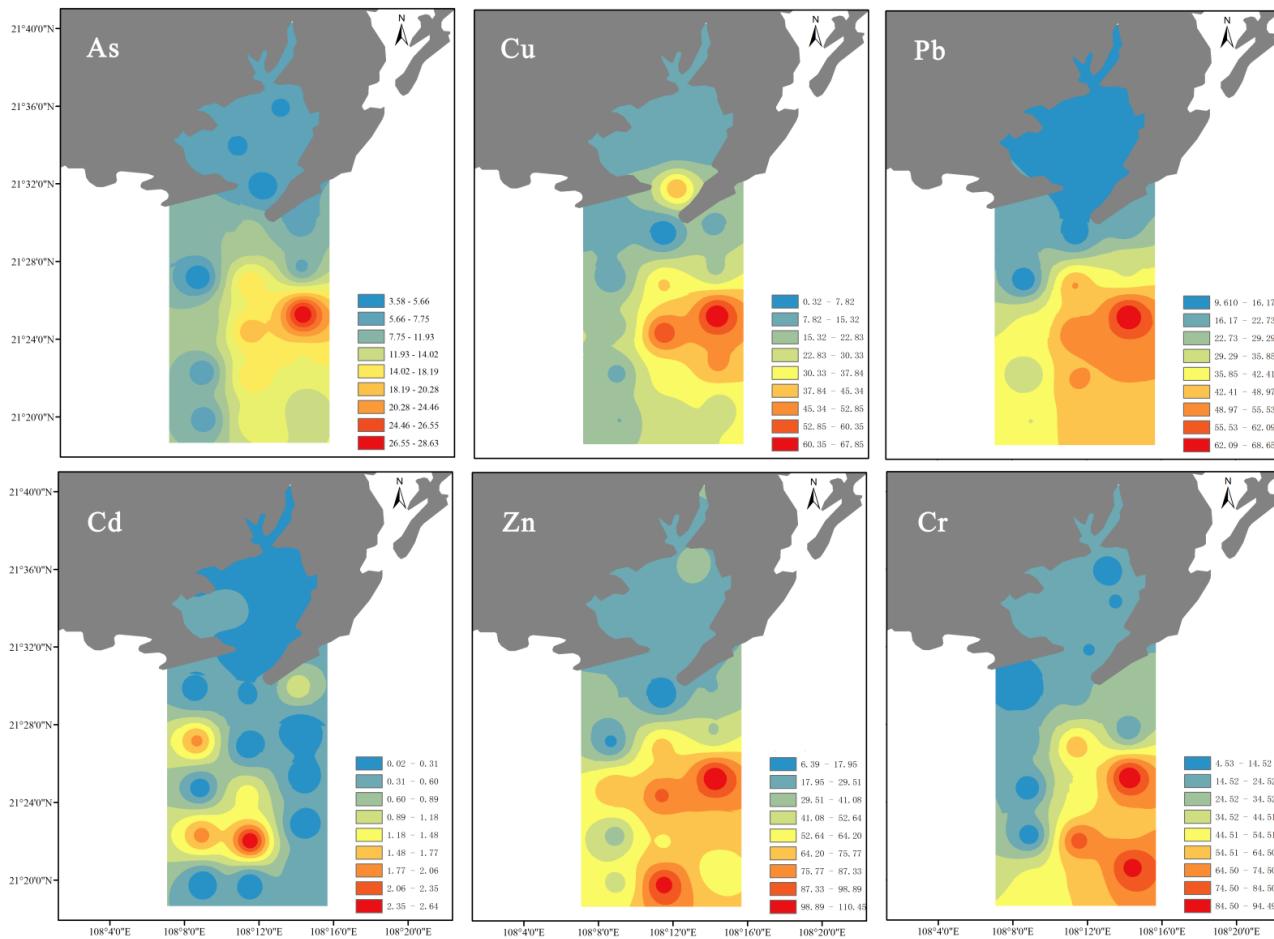


Figure 2. Spatial distribution of heavy metals in the surface sediments of the coastal Pearl Bay.

Until now, studies focusing on the heavy metals in the sediments of Pearl Bay were not available. Thus, we extracted several data information on metal concentrations from other works near this area to investigate the temporal variation (Table 4). The results demonstrated that levels of Zn (62.37) and Pb (43.53) concentrations in 2020 were comparatively higher than those values of this study, with the rest four metals showing a slightly increasing trend of metal concentrations in recent years [23]. Compared with the earlier

phase (year 2013), the present study exhibited a considerably higher concentration profile of Cu, As, Cd, and Pb [13]. It is worthy to note that both of the two latest Cd concentrations (including the data of the present study) were significantly higher than the corresponding value reported in 2013, indicating a rapidly growing trend of this toxic metal recently. In the coastal Pearl Bay, the increasing trend of heavy metal accumulation in sediments is likely influenced by intensive discharges of human activities, such as aquaculture input, agricultural runoff, vehicle emission, and electroplating factories [23].

3.3. Source and Transport of Heavy Metals

Principal component analysis (PCA) was used to analyze the study the relationships between the selected heavy metals in the surface sediments of Pearl Bay. The rotated component matrixes of the PCA are presented in Table 5. Two principal components (PCs) with eigenvalues > 1 were taken out as a consideration. Generally, metal concentrations in surface sediments exhibited a clear gradient along the main axis. PC1 explained 68.945% of the total variance and was dominated by Pb ($R = 0.961$) and As ($R = 0.943$), with the highest eigenvalue being 4.137. PC2 was dominated by Cd ($R = 0.994$), and accounted for 17.044% of the total variance with an eigenvalue of 1.023. Negative correlations of the metal elements between PCs one and two indicated that there might be two different models of metal sources in the sediments.

Table 5. Principal component analysis indexes of heavy metals.

Metal Elements	PC1	PC2
As	0.943	-0.019
Cu	0.861	-0.069
Pb	0.961	0.043
Cd	0.054	0.994
Zn	0.917	-0.124
Cr	0.859	0.112
Eigenvalue	4.137	1.023
Variance (%)	68.945	17.044
Cumulative of variance (%)	68.945	85.990

The Person correlation (PC) matrix is commonly used to find a common source of metal [19], thus the relationships among the examined heavy metals were verified using this method in the present study. Table 6 presents the PC matrixes of heavy metals in the surface sediments of Pearl Bay. There were high correlations among metals of As, Cu, Pb, Zn, and Cr, indicating that these metals might have common anthropogenic sources. Contrarily, Cd was observed to have no correlations with the above-mentioned metals, suggesting a different inputting channel of Cd. The heat map according to hierarchical cluster analysis showed the same relationships among the six studied metal elements (Figure 3). Moreover, the sites of Area I (S1–S4) and three sites (S1–S4) in Area II clustered together in one group, indicating the similar metal source and distribution patterns in sediment samples of these two areas. Previous studies have demonstrated that heavy metals in sediments were probably introduced from different anthropogenic and natural sources [34–36]. The possible sources of Cu, Zn, and Cr may originate from natural sources inland. Pb and As may come from the gasoline and diesel fuel from engine boats. The relative enrichment of Cd may be caused by the high input of phosphate fertilizers used in agricultural activities and phosphate mining nearby [13,21,23,27]. Concerning this, it is necessary to develop organic agriculture and green aquaculture as well as reduce the number of high contaminative industries around Pearl Bay, to control and minimize the anthropogenic metal inputs from the primary source.

Table 6. Pearson correlation coefficient matrix of heavy metals and TOC in surface sediments of the coastal Pearl Bay.

	TOC	As	Cu	Pb	Cd	Zn	Cr
TOC	1						
As	0.626 **	1					
Cu	0.525 *	0.774 **	1.000				
Pb	0.615 **	0.877 **	0.77 **	1			
Cd	0.417	0.030	-0.010	0.095	1		
Zn	0.57 **	0.834 **	0.739 **	0.91 **	-0.051	1	
Cr	0.663 **	0.793 **	0.645 **	0.796 **	0.113	0.679 **	1

* Correlation is significant at the 0.05 level (2-tailed). ** Correlation is significant at the 0.01 level (2-tailed).

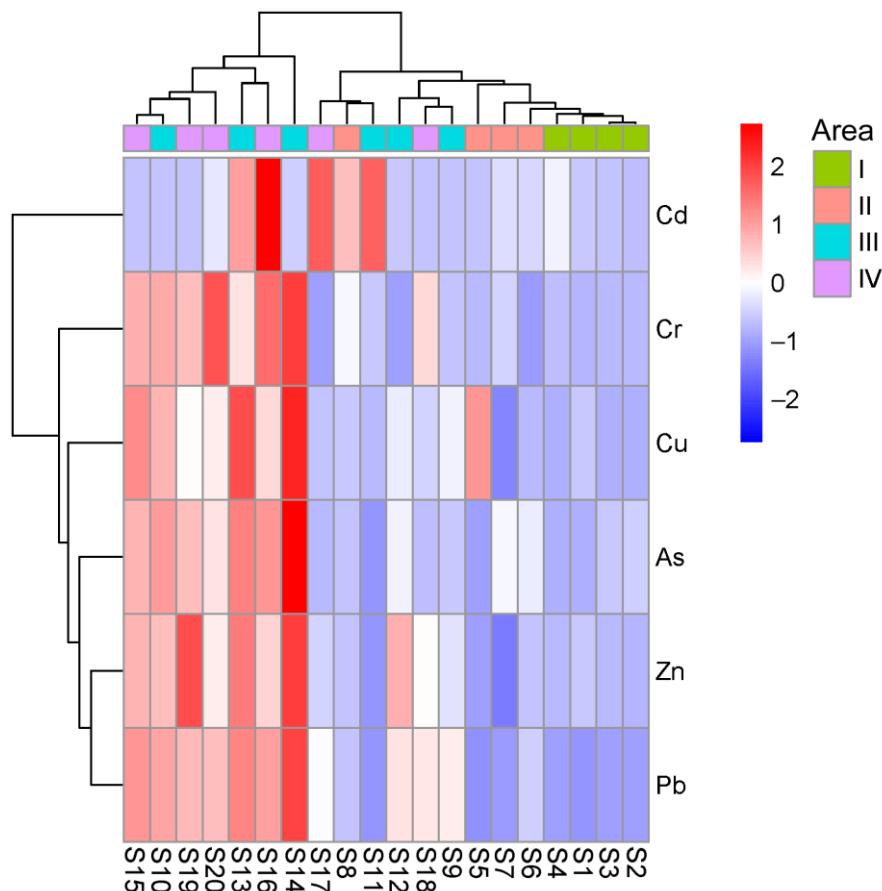


Figure 3. Hierarchical clustering map of the studied heavy metals in sediments of the coastal Pearl bay.

3.4. Risk Assessment

The I_{geo} values for the study area are presented in Table 7 and Figure 4. In total, I_{geo} values followed the order as: Cu > Pb > Cd > As > Zn > Cr. Among those, the average I_{geo} values of Cu and Pb were > 0, indicating that there were exogenous inputs of these two metals around the study area. Except for Cu at site S1 and Cd at site S4, all the remaining I_{geo} values of the six tested heavy metals in sediment of inner Pearl Bay (Area I) were below zero, representing the category ‘Practically unpolluted’ at S1–S4 sampling area. In Area II, site S5 and S8 were considered moderately to highly polluted, since these two sites showed high I_{geo} value of Cu (2.01) and Cd (2.03), respectively. The average I_{geo} values of Area III ranged from -1.00 (Cr) to 1.42 (Cu), indicating that site S11 was moderately polluted by Cu. Similarly, the calculated I_{geo} indexes showed that Area IV stations were polluted by Cu, Pb, and Cd, with I_{geo} values being 1.12, 0.86, and 0.18, respectively. The high values of I_{geo} for

Cu might be partly due to the low background Cu level in the study area [37]. Actually, the measured Cu concentrations were far lower than the SQGs used by the National Oceanic and Atmospheric Administration (NOAA) [38].

Table 7. I_{geo} values for metals in the sediment samples of the coastal Pearl Bay.

Station	As	Cu	Pb	Cd	Zn	Cr
S1	-1.46	0.28	-1.11	-1.17	-1.38	-2.15
S2	-0.97	-0.50	-0.91	-3.75	-1.75	-2.06
S3	-1.00	-0.49	-0.94	-2.75	-1.66	-1.94
S4	-1.47	-0.49	-0.93	0.74	-1.59	-1.87
S5	-1.77	2.01	-1.28	-2.43	-2.12	-2.09
S6	-0.62	-0.13	-0.10	-0.30	-1.46	-3.70
S7	-0.48	-5.12	-0.97	0.00	-3.67	-1.42
S8	-1.10	0.23	-0.26	2.03	-1.48	-0.82
S9	-1.02	0.92	0.58	-2.17	-1.02	-1.75
S10	0.30	1.80	1.08	-1.75	-0.25	0.05
S11	-2.02	-0.10	-1.08	2.78	-2.41	-1.58
S12	-0.54	0.87	0.66	-1.30	-0.14	-3.01
S13	0.43	2.41	1.23	2.30	0.15	-0.40
S14	0.98	2.61	1.55	-0.85	0.44	0.68
S15	0.13	2.08	1.16	-1.75	-0.17	0.04
S16	0.31	1.52	1.10	3.29	-0.37	0.43
S17	-1.30	0.20	0.40	2.81	-1.21	-2.98
S18	-1.18	0.45	0.61	-1.95	-0.71	-0.33
S19	0.07	1.16	0.95	-1.75	0.36	-0.10
S20	-0.20	1.31	0.92	0.45	-0.59	0.59
Average	-0.65	0.55	0.13	-0.38	-1.05	-1.22
Area I	-1.23	-0.30	-0.97	-1.74	-1.59	-2.00
Area II	-0.99	-0.75	-0.65	-0.18	-2.19	-2.01
Area III	-0.31	1.42	0.67	-0.16	-0.54	-1.00
Area IV	-0.36	1.12	0.86	0.18	-0.45	-0.39

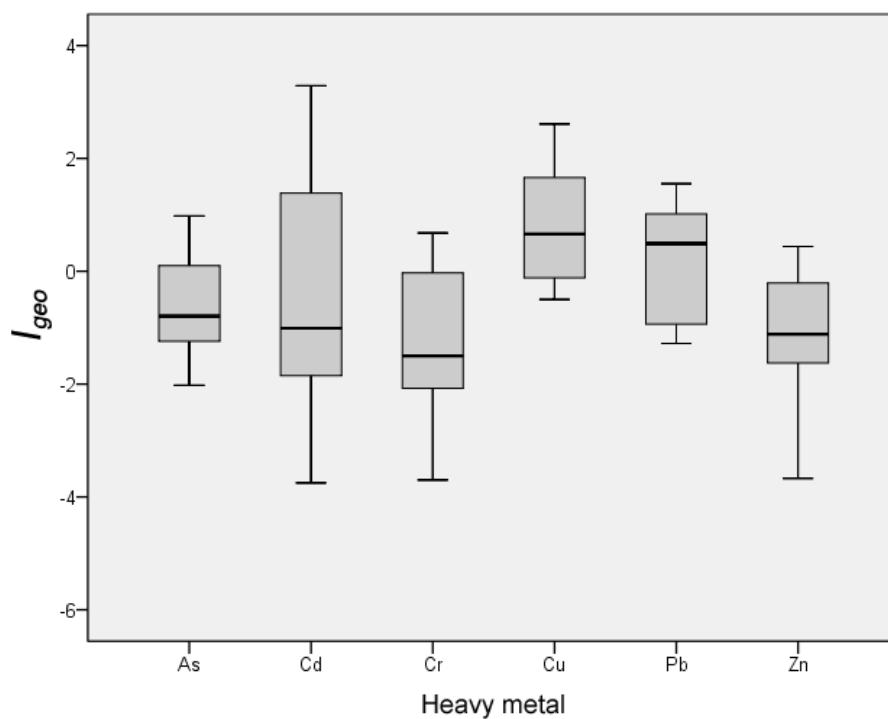


Figure 4. Geo-accumulation index (I_{geo}) of heavy metals in the surface sediments of the coastal Pearl Bay.

The single pollution index provides a simple, comparative means for assessing the level of heavy metal pollution, with CF value > 1 indicating a polluted condition, while CF value < 1 suggesting no metal pollution events [39]. In the present study, CF values of Zn for all investigated sites were detected as <1, which suggests a sign of low contamination by Zn. The average CF values of As, Cu, Pb, and Cr were 0.54, 0.69, 0.52, and 0.45, respectively. However, Cd showed high CF values at sites S16 (5.30), S17 (3.80), and S11 (3.72), which are all in the range of 3–6. Consequently, these sites were tagged as considerably contaminated by Cd.

According to the potential ecological risk index, studied metals were arranged as: Cd > Cu > As > Pb > Cr > Zn (Table 8). The E_r^i values of the sampling stations around Pearl Bay were at low ecological risk by As, Cu, Pb, Zn, and Cr, since the E_r^i values were lower than 40. However, E_r^i values of Cd in sediments of S16 (159.0), A17 (114.0), and S11 (111.6) were >80, indicating a considerable ecological risk of Cd. Meanwhile, E_r^i values of Cd at sites S13 and S8 were observed larger than 40, suggesting moderate ecological risk (Figure 5). Though the average E_r^i value of Cd was calculated under the guideline of low ecological risk, two stations in Area IV were found with extremely high E_r^i values (51.50), leading to a moderate Cd risk in this study area. Cd is much more toxic and can be accumulated throughout human life and may cause some diseases, such as kidney dysfunction and reproductive deficiencies [40]. The observations of this study demonstrated that Cd contamination was obvious in coastal areas of Pearl Bay, especially in the south region of the study area. Similar to our results, Cd contamination was also recorded in surface sediments from the Thondi coast, Palk Bay, South India, with the anthropogenic inputs such as municipal wastewater, domestic sewage discharge, fishing harbor activities, and industrial and aquaculture wastes being considered to be the potential sources [41]. According to previous studies [22], moderate pollution of Cd was also reported in the north of the eastern Beibu Gulf. The elevated Cd values in coastal areas of Beibu Gulf were considered to be caused by the presence of anthropogenic pollution transported by the rivers such as Bei Lun, Mao Ling, and Da Feng Rivers [42].

Table 8. E_r^i and RI values for heavy metals in sampling sites of the coastal Pearl Bay.

Station	E_r^i						RI
	As	Cu	Pb	Cd	Zn	Cr	
S1	1.33	1.93	0.91	7.20	0.21	0.33	11.91
S2	1.86	1.12	1.04	1.20	0.16	0.35	5.73
S3	1.82	1.13	1.01	2.40	0.17	0.38	6.92
S4	1.31	1.14	1.03	27.00	0.18	0.40	31.06
S5	1.07	6.42	0.80	3.00	0.12	0.35	11.75
S6	2.38	1.45	1.82	13.20	0.20	0.11	19.16
S7	2.62	0.05	0.99	16.20	0.04	0.55	20.45
S8	1.70	1.87	1.63	66.00	0.19	0.84	72.23
S9	1.80	3.02	2.91	3.60	0.27	0.44	12.04
S10	4.49	5.53	4.11	4.80	0.46	1.52	20.90
S11	0.90	1.49	0.92	111.60	0.10	0.49	115.50
S12	2.51	2.91	3.09	6.60	0.49	0.18	15.78
S13	4.89	8.46	4.59	79.80	0.60	1.12	99.46
S14	7.16	9.69	5.72	9.00	0.74	2.36	34.68
S15	4.00	6.73	4.36	4.80	0.48	1.51	21.88
S16	4.51	4.58	4.19	159.00	0.42	1.99	174.68
S17	1.48	1.83	2.57	114.00	0.23	0.19	120.30
S18	1.60	2.18	2.98	4.20	0.33	1.17	12.47
S19	3.81	3.57	3.77	4.80	0.70	1.37	18.02
S20	3.18	3.95	3.69	22.20	0.36	2.21	35.59
Average	2.72	3.45	2.61	33.03	0.32	0.89	43.03
Area I	1.58	1.33	1.00	9.45	0.18	0.37	13.90
Area II	1.94	2.45	1.31	24.60	0.14	0.46	30.90
Area III	3.62	5.18	3.56	35.90	0.44	1.02	49.73
Area IV	3.10	3.81	3.59	51.50	0.42	1.41	63.82

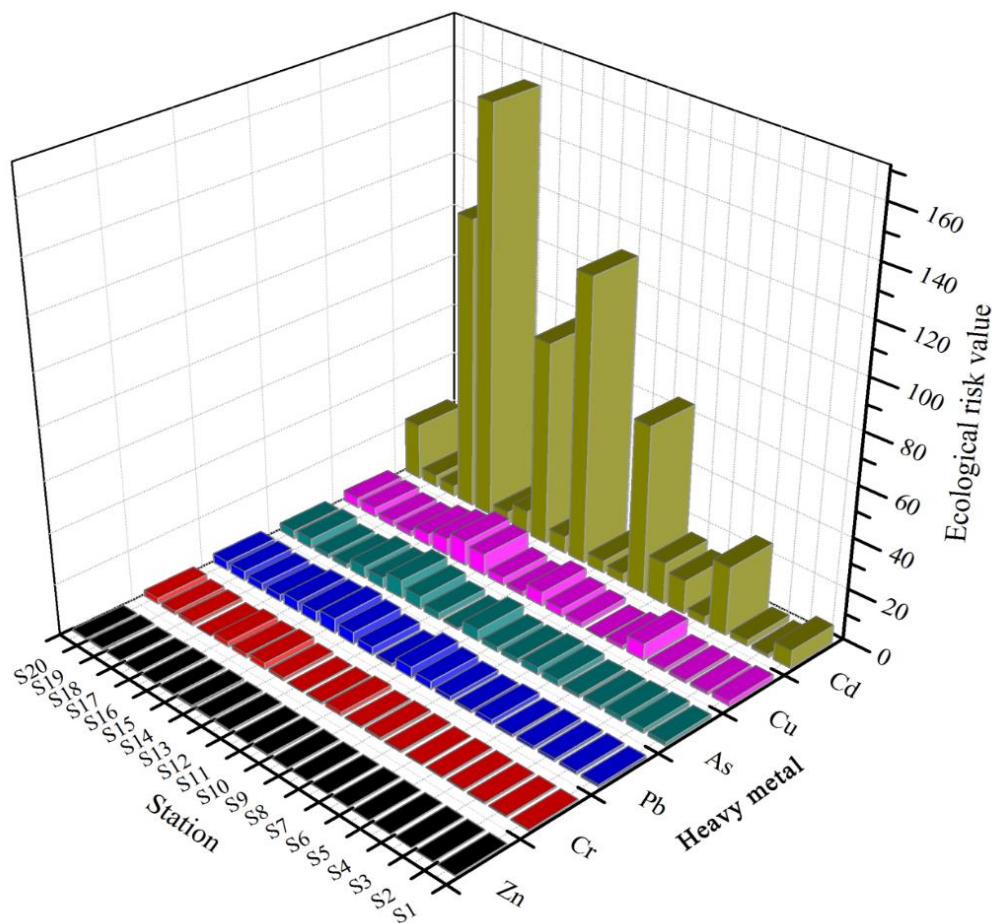


Figure 5. E_r^i values of heavy metals at all sediment sampling sites in the coastal Pearl bay.

In the present study, RI was determined as another indicator to assess the potential ecological risk of heavy metals (Table 8). Overall, the RI values of the 20 investigated sediment samples ranged from 5.73 to 174.68. The result leads to a decision that the examined heavy metals posed low ecological risks to the surface sediments of Pearl Bay. As it was mentioned above, the sediment of site S16 was considerably polluted by Cd, resulting in moderate ecological risk at this site. Similar to our results, Dou et al. (2013) pointed out that the sediment of eastern Beibu Gulf had no ecological risk when excluding Cd pollution [22]. However, contaminant behavior in sediments is a dynamic process and can be regulated by various physical and chemical factors, thus chemical analyses alone do not necessarily reflect the actual toxic action of contaminants [43]. Therefore, further research is recommended to focus on finding out the accurate source of Cd and studying its transmission pattern in the aquatic ecosystem of Pearl Bay. Additionally, the integrated and multidisciplinary approaches such as the Weight Of Evidence (QOE) method, Lines Of Evidence (LOEs) chemical analyses, contaminant recognition method [44], and geo-chemo-mechanical methodology [45] are required to comprehensively evaluate and classify the chronically biological, chemical and toxicological impacts of the contaminants in the study area.

4. Conclusions

In the present study, heavy metals of twenty surface sediment samples collected from the coastal Pearl Bay (South China Sea) were measured to determine their concentration levels, distribution patterns, potential sources, and ecological risks. Overall, the metal concentrations in sediments of the study area meet the Grade I standard of China Marine Sediment Quality excepting Cd. The high I_{geo} , CF, and E_r^i index values of Cd indicate that potential Cd pollution may occur in the sediments of the present study region. According

to the distribution pattern of principal components, natural land input and anthropogenic sources are considered to be the main metal source models. PCA results show that 68.945% of the total variance loaded on Pb and As, suggesting a similar origin between these two metals. The Cd contamination may be primarily attributed to the high input of phosphate-related agricultural and mining activities nearby.

Author Contributions: Conceptualization, C.Y.; data curation, C.Y. and G.Y.; formal analysis, Y.L.; funding acquisition, D.S. and Y.H.; investigation, B.S.; validation, L.W.; visualization, B.S. and L.W.; writing—original draft, C.Y.; writing—review and editing, C.Y. and Y.H. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the Open Foundation of Guangdong Provincial Key Laboratory for Healthy and Safe Aquaculture (No. GDKLHSA1905), the Central Public-interest Scientific Institution Basal Research Fund, South China Sea Fisheries Research Institute, CAFS (No. 2021SD14), the Ministry of Agriculture and Rural Affairs Special Fund Project (No. 2021–125A0501), and the special Fund Project of Guangdong Province (No. 2020–0103020203048).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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