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Distribution of Heavy Metals in Surface Sediments of a Tropical Mangrove Wetlands in Hainan, China, and Their Biological Effectiveness

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Abstract: The distribution and ecological risk of heavy metals in sediments were studied through the systematic collection and analysis of mangrove wetland sediments in Dongzhai Harbor, Hainan. The main insights obtained were as follows: (1) The distribution characteristics and influencing factors of heavy metals in wetland sediments were analyzed by using the inverse-distance weight interpolation method. In terms of spatial distribution, the contents of heavy metals As, Ba, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Sr, Ti, and Zn in the western part of the wetland were significantly higher than in the eastern part. The contents of heavy metals Cd, Co, Cr, Cu, Hg, Mn, Ni, Zn, and Ti near the anthropogenic area were significantly higher than at other points. (2) The pollution sources and ecological risks of heavy metals in wetland sediments were explored by using correlation analysis, cluster analysis, and potential ecological risk index analysis. The results showed that As, Ba, Pb, and Sr mainly originated from natural processes; Co, Cr, Cu, Mn, Ni, Ti, and Zn mainly originated from industry; and agricultural heavy metals mainly originated from Cd and Hg. The ecological risk analysis showed that there were obvious ecological risks of heavy metals in the western and southeastern corners of the wetland, which were both located in the vicinity of land far away from the coastline and near the human activities, and featured mangrove forests with dense vegetation characteristics.

Keywords: sediment; mangrove; heavy metal; pollution; Dongzhai Harbour

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1. Introduction

Mangrove forests are intertidal forests that grow on warm temperate, subtropical, and tropical coastlines and form adjacent waterways [1,2]. Mangrove wetlands, as "marine forests", are of great practical significance in terms of coastal protection, biological survival, and socio-economic development [3,4]. Since the 1980s, 70% of the world's coastal zones have been subjected to anthropogenic pressures, and coastal zone pollution has been increasing [5]. Although mangrove wetland systems can receive many pollutants carried from tides, rivers, surface runoff, etc., they have also become an important source of pollution, causing environmental degradation problems to local sediments and even wetland ecosystems [6]. Among them, heavy metals are characterized by their accumulation and biomagnification in ecosystems and do not easily decompose and degrade, which can easily affect the stability of the environment and ecosystems [7]. For example, mangrove forests in the state of Alagoas, Brazil, have been contaminated by sediment enrichment of heavy metals, such as Mn, Zn, Pb, Cr, Cu, and Cd, due to the discharge of domestic sewage and agricultural and industrial wastewater [8]. The mangrove forests of Estrozarado on the northwest coast of South America have been affected by the release of industrial wastewater for a long time, and the heavy metals Pb, Sn, Cd, Ag, Mo, Zn, and Ni have been heavily enriched in the sediment, which has become one of the most damaged mangrove ecosystems on Earth [9]. As the largest developing country in the world, China has been experiencing increasing pollution from heavy metals with its rapid economic development.

Mangrove forests are in the sensitive intertidal zone where land and sea meet, and their ecological environment is controlled by the dual influence of the sea and the land. The environmental pressure on mangrove wetlands is increasing due to the increase in the population, the development of industrial and agricultural production in cities and watersheds, and especially the extensive selection of bay estuaries as sewage disposal sites for coastal cities, which has led to a large amount of pollutants entering the estuarine area [10,11]. In 2020, Mao et al. [12], through the analysis of nine heavy metals in mangrove wetland sediments in Dongzhai Harbor, found that the content of heavy metals such as Cd, Cr, Cu, Ni, Zn, and Co in this area exceeded the standard, and the potential ecological risk and the quality of the concentration of the multiple possible impacts showed that the area with high concentrations of heavy metals and the surface of the sediment in the range of 0–20 cm were more susceptible to contamination by heavy metals. Studies have shown that the distribution of heavy metals in mangrove wetland sediments is closely related to changes in land-use patterns [13]. Li et al. [14] also concluded that shifts in land use in mangrove forests on Hainan Island have altered the sediment's ability to accumulate heavy metals, bringing varying degrees of heavy metal contamination to wetlands. In conclusion, focusing on the spatial distribution of heavy metals in sediments, exploring the impact of heavy metals in sediments on the environment, and investigating the main sources of heavy metals in sediments are of great significance for the protection of wetland ecology and the sustainable development of coastal areas [15].

Based on previous investigations of heavy metals in sediments, most of the studies on mangrove wetlands in this area have focused on the content and ecological risk assessment of heavy metals in estuarine bays, but few studies on biological effectiveness have been reported [16–19]. In addition, studies on both the sources and ecological risks of heavy metals in tropical mangrove forests are uncommon. The present study was conducted to comprehensively analyze 13 major heavy metal pollutants in the mangrove sediments of Dongzhai Harbor, Hainan Province, including As, Ba, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Sr, Ti, and Zn. The main purpose was to analyze the spatial distribution, ecological risk, main sources, and main control factors of heavy metals in the sediments of mangrove wetlands in Dongzhai Harbor, Hainan, to provide a scientific basis for the control of heavy metal pollution in mangrove forests and ecosystem protection.

2. Materials and Methods

2.1. Study Area

Dongzhai Harbor Mangrove Wetland is in Haikou City, Hainan Province, northeast of Hainan Island, with a tropical maritime monsoon climate. The average annual temperature is 17.1 °C, the average annual precipitation is 1676 mm, and the all-weather irregular tides have an average tidal range of approximately 1 m (Figure 1) [12]. Dongzhai Harbor is a drowned-valley-type harbor formed by the collapse of the 1605 Qiongshan earthquake, and is injected by small streams such as the Zhuxi River, Qiaotou River, and Yanfeng River. Mudflats formed by sediments provide habitats for ecosystems and conditions for heavy metal enrichment [20]. The topography of the harbor coast is flat and the lithology is dominated by granite [21]. The area is dominated by loose Quaternary sediments, which are the main source of sediments in the harbor [22]. In recent decades, industrial and agricultural development has been rapid. The overall land for construction in Dongzhai Harbor has grown dramatically, and forest land has been reduced in large areas. The total area of wetlands is approximately 360 km^2, and the main land-use types are paddy field, forest land, construction land, mudflat, and water system. Agricultural land and forest land account for the largest land-use proportion of the wetland, both of which account for approximately 50% of the total area; the three types of rivers, mudflats, and construction land account for more than 30% of the total area of the wetland. The main economic sources of the nearby residents are agriculture and fisheries. Farming ponds distributed along the shoreline directly discharge wastes such as farm wastewater and substrate into the mangrove wetland.

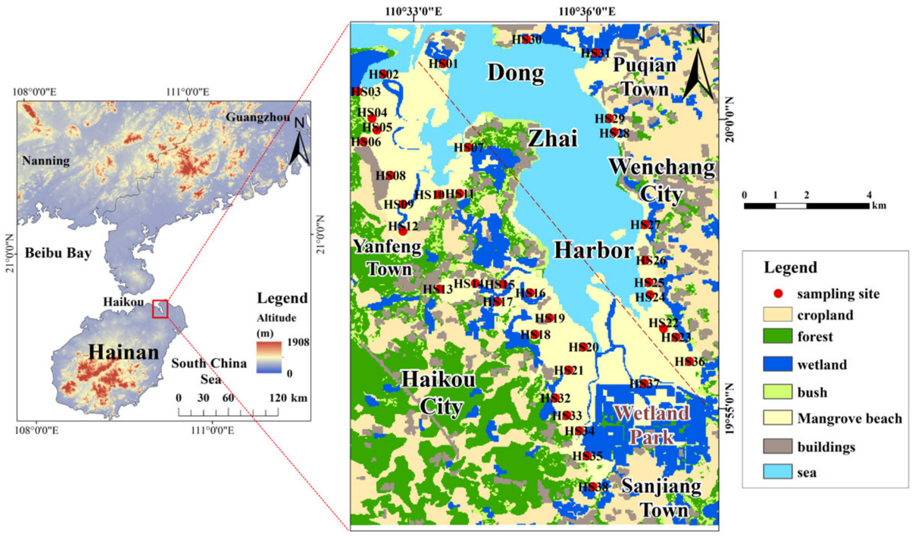


Figure 1. The locations of the sampling sites.

2.2. Sample Collection and Analysis

Based on the field survey, a total of 38 samples of topsoil (0–30 cm) were collected from various points (HS01–HS38). Sediment samples were taken and stored in clean polyethylene bags using an auger tool and numbered with a marker pen, with the number corresponding to the point number (HS01–HS38).

The sediments were dried, ground, and sieved (100 mesh nylon sieve) for spare parts. The particle size distribution was determined using a laser particle sizer (Mastersizer 2000, Malvern Panalytical, Malvern, UK) with an accuracy of better than 1%; the organic carbon (C_{org}) content was determined using an elemental analyzer (VarioMacro-CHNS, Langenselbold, Germany) with an accuracy of 0.5%; and nitrogen (N), phosphorus (P), silicon dioxide (SiO_2), aluminum trioxide (Al_2O_3), magnesium oxide (MgO), calcium oxide (CaO), sodium oxide (Na_2O), potassium oxide (K_2O), and other macronutrients were determined using X-ray fluorescence spectrometry (XRF), for which the detection limit of the instrument was 1 mg/kg and the analytical precision was 0.02%~2.0%; the pH value was determined using a Mettler Delta 320 pH (Mettler Toledo Delta 320, Mettler-Toledo Inc., Greifensee, Switzerland) with an accuracy of $\pm$ 1. The content of heavy metal elements and iron was determined using inductively coupled plasma mass spectrometry (ICP-MS), with an accuracy of 2%~4%. The analyzed data were assessed for accuracy and precision using quality assurance and quality control (QA/QC) measures, which included reagent blanks, duplicate samples, and certified reference materials. The detailed analytical procedures are introduced in Li et al. [22]. Before the determination, the samples were dissolved to a mixture of 10 mL HCl (ρ = 1.19 g/mL), 10 mL HNO_3 (ρ = 1.42 g/mL), 10 mL $HClO_4$ (ρ = 1.68 g/mL), and 10 mL HF (ρ = 1.49 g/mL).

2.3. Statistical Analysis

The tabulation of the data obtained from the experiment was performed using Word and Excel. SPSS 23 and Origin 2021 were used for data processing, correlation analysis, and cluster analysis. Ecological risk assessment of heavy metal content in sediments was performed using the potential ecological risk assessment (PERA) method and the Nemero index (NI) method. Descriptive statistics were used to observe trends in the dataset. The relationship between the metals (samples) was evaluated u Pearson correlation coefficient. To test the suitability of the principal component data, the Kaiser–Meyer–Olkin (KMO) test was used. The KMO test calculates sampling adequacy, i.e., the proportion of variance that is likely to be normal variance among the variables investigated. Patterns of toxic metals in sediments were assessed using cluster analysis of Euclidean distance matrices, which were assigned with heat maps.

2.4. Risk Assessment Methods

In this study, we used single potential ecological risk index (E_r^i), potential ecological risk index (RI), and Nemero pollution index for ecological risk evaluation to achieve a comprehensive analysis of the possibility of heavy metal pollution. The methodology is detailed in Table 1.

Table 1. Risk evaluation expression and physical significance.

Name	Expression	Coefficient of Interpretation	Classification and Contamination Degree	Reference
Individual potential ecological risk index (E_r^i)	$E_r^i = T_r^i \times \frac{C_i}{C_{ref}}$	${T^i}_r$: Toxicity coefficient, according to previous research results, the toxicity response coefficients of Hg, Cd, As, Cu, Pb, Ni, Cr, Co, and Zn are 40, 30, 10, 5, 5, 5, 2, 2, and 1, respectively. C_i: The measured content of element i in sediments (mg/kg). C_{ref}: The geochemical background value of element n (mg/kg).	$E_r^i < 40$: Low risk $40 \leq E_r^i < 80$: Moderate risk $80 \leq E_r^i < 160$: Heavy risk $160 \leq E_r^i < 320$: Serious risk $E_r^i \geq 320$: Extremely serious risk	[23]
Potential ecological risk index (RI)	$RI = \sum_{i=1}^{n} E_r^i$	E_r^i: Individual potential ecological risk index.	RI < 150: Low risk 150 < RI ≤ 300: Moderate risk 300 < RI ≤ 600: Serious risk RI > 600: Extremely serious risk	[24]
Nemerow pollution index (PN)	$PN = \sqrt{\frac{CF_{ave}^2 + CF_{max}^2}{2}}$	CF_{ave}: The average of contamination factors of investigated metals. CF_{max}: The maximum contamination factor for a metal in a sample.	PN ≤ 0.7: Safe 0.7 < PN ≤ 1: Warning 1 < PN ≤ 2: Mild contamination 2 < PN ≤ 3: Moderate contamination PN > 3: Serious contamination	[25]

3. Results

3.1. Spatial Distribution of Physico-Chemical Properties

Since Wenchang City and Haikou City in Hainan Province have some differences in economic development and natural conditions, this paper divides the study area into two parts: east (Wenchang City) and west (Haikou City) (Figure 1). The textural classification of the sediment samples was based on the relative percentages of clay (<4 μm), silt (4–63 μm), and sand (63–2000 μm), according to the Udden–Wentworth grade scale (Wentworth, 1922). The content of sand, silt, and clay ranged from 10.21% to 90.20%, 7.21% to 74.50%, and 2.60% to 20.30%, respectively; the mean ranking was silt (55.96%) > sand (32.56%) > clay (11.48%). The wetland sediments were mainly composed of silt and sand (Table 2). The sediment grain size composition was similar to the Hainan background values given in the 1990 Chinese Soil Elemental Background Values [26].

The wetland sediment pH spanned a wide range from 4.05 to 8.19, but the overall performance was weakly acidic (Table 2). The pH coefficient of variation was approximately 14%, with low spatial differentiation, and it was less influenced by the natural environment. The high pH sites were all in the terrestrial areas close to the coastline, while the low pH sites were mainly distributed in the mangrove woodlands away from the coastline.

In the study area, the content of C_{org}, N, and P varied (mg/kg) from 2000 to 40,500, 205 to 2617, and 146 to 2078, respectively, with mean values of 15,300 mg/kg, 1015 mg/kg, and 671 mg/kg, respectively, and the average content exceeded the background value in Hainan Province [26] (Table 2). The coefficients of variation for C_{org}, N, and P in the study area were greater than 50%, which is a strong variation. In terms of spatial distribution, the nutrient salt content was much higher in the densely vegetated mangrove area and inland areas such as HS35 and HS38 than at other points. Construction land was located near HS35 and HS38 [11]. It was inferred that the distribution of C_{org}, N, and P content in the wetland was greatly influenced by anthropogenic activities.

Table 2. Descriptive statistics for particle size and pH data.

Area	Content	Sand (%)	Silt (%)	Clay (%)	pH	C_{org} (mg/kg)	N (mg/kg)	P (mg/kg)
East	Min.	14.50	7.20	2.60	4.89	2000	205.00	146.00
	Max.	90.20	74.50	13.50	8.19	28200	1935.00	1024.00
	Average	37.63	52.29	10.08	7.05	9900	754.00	497.00
	Standard deviation	18.68	17.01	3.41	0.99	8400	539.69	261.23
	CV (%)	49.63	32.54	33.8	14.1	84.59	71.58	52.62
West	Min.	10.20	40.10	4.40	4.05	4300	342.00	264.00
	Max.	51.20	70.90	20.30	7.70	40500	2619.00	2079.00
	Average	29.92	57.87	12.21	6.18	20600	1276.00	845.00
	Standard deviation	13.61	10.64	4.89	0.91	9400	575.39	447.05
	CV (%)	45.48	18.39	40.05	14.75	45.69	45.11	52.92
Synthesis	Average	33.78	55.08	11.15	6.62	15250	1015.00	671.00

3.2. Spatial Distributions of Heavy Metals

Combined with the biotoxicity study of various heavy metals by Hakanson and Xu Zhengqi, 13 sediment heavy metals (As, Ba, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Sr, Ti, and Zn) in the wetland were selected in this paper [27,28]. The results of the statistical analysis of the content of the 13 heavy metal elements are shown in Table 3.

Table 3. Heavy metals content.

Area	Content	Heavy Metals Content (mg/kg)												
		As	Ba	Cd	Co	Cr	Cu	Hg	Mn	Ni	Pb	Sr	Ti	Zn
East	Min.	2.50	133.00	0.01	3.40	21.00	4.90	0.01	123.00	5.90	10.20	43.00	1716.00	22.00
	Max.	7.90	337.00	0.18	15.10	84.00	29.50	0.07	419.00	35.20	32.80	97.00	7221.00	90.00
	Average	5.19	254.00	0.07	8.27	52.00	14.19	0.03	239.00	18.54	20.67	76.00	4446.00	53.00
	Standard deviation	2.06	67.86	0.04	4.15	20.71	7.34	0.02	95.53	10.14	7.71	16.97	1728.40	23.01
	CV (%)	39.77	26.72	66.88	50.20	39.96	51.70	63.70	40.00	54.69	37.31	22.43	38.88	43.23
West	Min.	3.40	19.00	0.04	4.30	44.00	9.10	0.02	66.00	10.20	11.00	19.00	2201.00	32.00
	Max.	11.40	335.00	0.23	48.20	288.00	84.20	0.09	1580.00	141.1	30.70	100.00	26719.00	195.00
	Average	6.43	265.00	0.11	16.65	97.00	26.02	0.05	390.00	38.58	23.62	81.00	7951.00	82.00
	Standard deviation	2.10	77.38	0.05	9.87	53.73	16.02	0.02	294.48	26.03	5.14	19.92	5078.48	37.10
	CV (%)	32.62	29.18	42.63	59.27	55.42	61.57	36.64	75.58	67.46	21.77	24.71	63.87	45.16
Synthesis	Average	6.01	261.00	0.10	13.78	82.00	21.97	0.04	338.00	31.72	22.61	79.00	6751.00	72.00

Sediment sources influenced the spatial distribution of heavy metal content in surface sediments in the study area. The spatial distribution of As, Ba, Pb, and Sr was more similar in the wetland. The northern part of the wetland (HS01, HS30, HS31, etc.) had low concentrations of heavy metals in the area. The rest of the locations had obviously high concentrations (Figure 2). The mean contents of As, Ba, Pb, and Sr in the eastern part of the wetland (mg/kg) were 5.19, 254.00, 20.67, and 76.00, respectively, and the mean contents (mg/kg) in the west were 6.43, 265.00, 23.62, and 81.00, respectively, with little difference in the contents. The coefficients of variation (%) for As, Ba, Pb, and Sr in the east and west were not very different. They basically showed medium variability, and all of them were more evenly distributed and more strongly influenced by natural factors such as material sources and tides.

The mean contents (mg/kg) of Cd, Co, Cr, Cu, Hg, Mn, Ni, Ti, and Zn in the east and west are shown in Table 3. The mean contents of these nine heavy metal elements were higher in the west than in the east. Except for Cd and Hg, which were more specific at points HS22 and HS23, these nine elements were mainly concentrated at points HS13 and

HS38 in the western part of the study area, and their distribution was characterized by their proximity to the anthropogenic areas (Figure 3). The coefficients of variation (%) of Cd, Co, Cr, Cu, Hg, Mn, Ni, Ti, and Zn in the eastern part of the study area were 66.88, 50.2, 39.96, 51.70, 63.7, 40.00, 54.69, 38.88, and 43.23, respectively, and in the west the coefficients of variation (%) were 42.63, 59.27, 55.42, 61.57, 36.64, 75.58, 67.46, 63.87, and 45.16, respectively. Generally, the greater the degree of disturbance of the physicochemical properties of the sediments caused by human activities, the higher the value of coefficient of variation [29]. The combination of the spatial distribution characteristics of heavy metals and the analysis of the coefficient of variation showed that the spatial distribution of heavy metals in the east and west of the wetland was strongly disturbed by human factors.

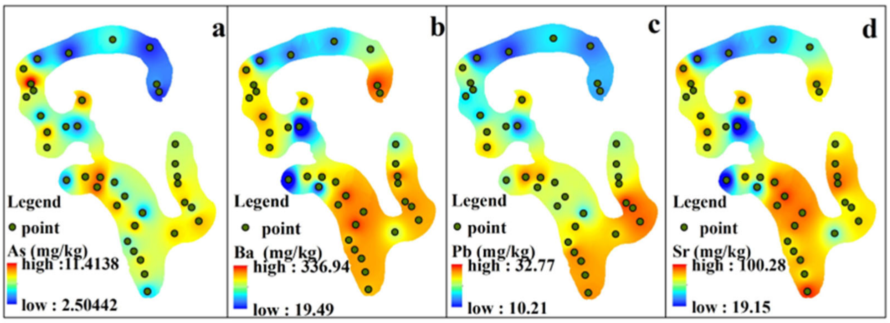


Figure 2. Characterization of the distribution of As (**a**), Ba (**b**), Pb (**c**), and Sr (**d**) content in sediments.

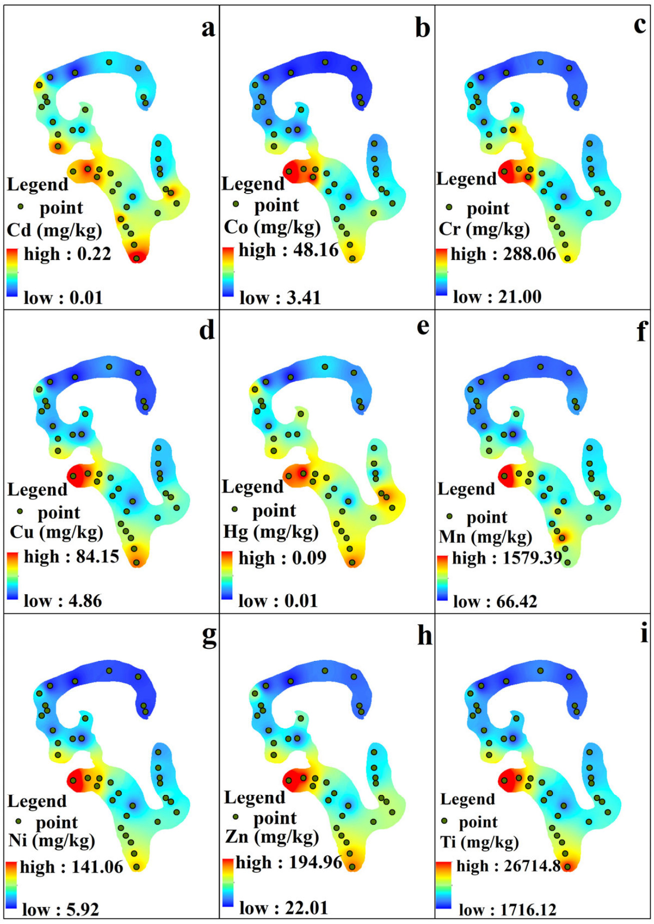


Figure 3. Characterization of the distribution of sediment Cd (**a**), Co (**b**), Cr (**c**), Cu (**d**), Hg (**e**), Mn (**f**), Ni (**g**), Ti (**h**), and Zn (**i**) contents.

4. Discussion

4.1. Source Apportionment of Metals in Sediment

A correlation analysis of the main physicochemical properties and heavy metal elements of the mangrove wetland sediments in Dongzhai Harbor, Hainan was carried out. The correlation between the elements is shown in Figure 4.

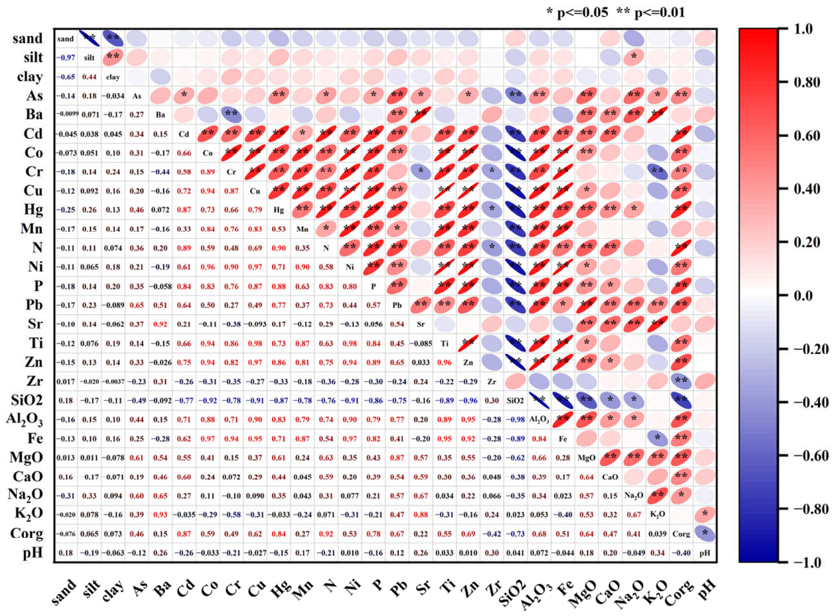


Figure 4. Correlation matrix of sediment trace elements and macronutrients.

There were no significant correlations between the heavy metals and sand, powder, and clay grains in Dongzhai Harbor mangrove forest. This suggests that the effect of the sediment grain size on heavy metal elements in the region is weak. This result did not conform to the “grain size control law of elements” [30].

There were highly significant positive correlations between the heavy metals Cd, Co, Cr, Cu, Hg, Ni, Pb, Ti, and Zn and the nutrient salts N, P, and C_{org}, with correlation coefficients greater than 0.5; As and Mn were significantly and positively correlated with the nutrient salts C_{org}, N, and P. The correlation coefficients between the heavy metals Cd and P were greater than 0.5. N, P, C_{org}, and other nutrients in sediments are not only conducive to the enrichment of heavy metals [31], but also form an important basis for identifying the source of organic pollution in the environment and sediments: when sediment C/N > 10, the source of organic matter is mainly exogenous; and if C/P and N/P are lower than the Redfield ratio (C:N:P 106:16:1), this indicated that the phosphorus in the sediment is mainly imported exogenously from the surrounding environment [24,32].

In this study, the mean values of C/N, C/P, and N/P were 15, 26, and 1.5, respectively, indicating that all nutrient salts in the wetland sediments were mainly exogenous inputs (Figure 5). The villages and towns around the mangrove wetland in Dongzhai Port are developing a business system based on agriculture and farming. The heavy metals contained in fertilizers and wastewater will be transported and deposited depending on the hydrological, topographic, and geomorphological conditions [13]. Xin et al. and Li et al. have also shown that, while the economy of Hainan is developing rapidly, many nutrient salts with heavy metals from industry and agriculture are discharged to the mangrove wetland of Dongzhai Port and deposited via the water system, atmosphere, and other pathway, which caused ecological health impacts to the wetland [13,14]. Therefore, agricultural sources may be one of the main sources of heavy metals in the sediments of the Dongzhaigang mangrove wetland.

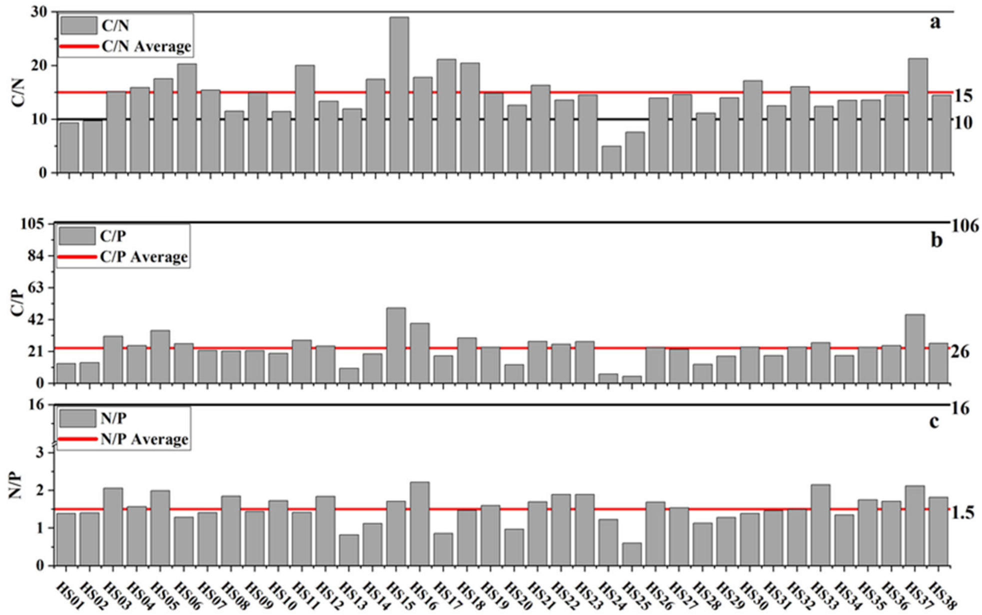


Figure 5. (**a**) Carbon and nitrogen ratios of mangrove wetland sediments in Dongzhai Harbor. (**b**) Nitrogen and phosphorus ratios of mangrove wetland sediments in Dongzhai Harbor. (**c**) Nitrogen and phosphorus ratios of mangrove wetland sediments in Dongzhai Harbor.

The correlation analysis also showed that SiO_2 showed a highly significant negative correlation with As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Ti, and Zn, and no significant correlation with Ba and Sr. Al_2O_3 showed a highly significant positive correlation with As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Ti, and Zn, which indicated that the heavy metal elements had a more consistent source of Al_2O_3 (Figure 5). Since there was no significant correlation between Al and either powder or clay grains, the significant positive correlation between Al and these heavy metals did not reflect the effect of particle size sorting on the content of these heavy elements. Al_2O_3 is a product of the physical weathering of continental rocks and is relatively stable in modern structures. In addition, Al_2O_3 is a major component of sediments and can be used as an indicator of the source [33]. Therefore, the 11 heavy metals were from natural sources. However, according to the analysis in the previous sections, the contents of Ba, Cd, Co, Cr, Cu, Mn, Ni, Sr, Ti, and Zn were higher than the background values, in which the average contents of Co, Cr, and Zn were nearly two times those of the background contents, and the average contents of the heavy metals Ni, Sr, and Ti reached nearly three times those of the background contents, and the neighboring villages and towns had intensive agriculture and fisheries [34]. Therefore, the industrial and agricultural production and other activities in the villages and towns around the wetland also provided a large contribution. MgO showed a highly significant positive correlation with As, Ba, Cd, Hg, Pb, Sr, Zn, and Al_2O_3. MgO represented the terrestrial source of clastic deposition, as did Al_2O_3. CaO showed a highly significant positive correlation but low correlation coefficients with Ba, Cd, Hg, Pb, and Sr. Ca is a marine characteristic element of biogenic sediments, representing biogenic calcium deposition, and Sr, as a pro-biotic element, is mainly enriched in coarse-grained biogenic shells and detritus [35]. According to the field geological characteristics, shells and corals are commonly seen in wetlands. Na_2O and K_2O showed highly significant positive correlations with As, Ba, Pb, and Sr (Figure 6). In general, Na_2O and K_2O mainly represent volcanic rock sources and marine chemical deposits. The northern part of Hainan Island experienced multiple phases of volcanic lava eruptions during the Quaternary period, and an uplifted basalt platform was formed along the coast [36,37]. The regional geological background shows that the lithology of the Duowen Formation (Qp^d2) in the western part of the wetland can be divided into upper and lower sections, representing a suite of basaltic lava formed during the Middle Pleistocene Duowen Ridge Stage and Dongying Stage, respectively, with volcanoclastic lavas visible near some of the craters, which represent fissure-centered eruptive volcanic facies. Thus, its origin is also controlled by natural sources (igneous rocks).

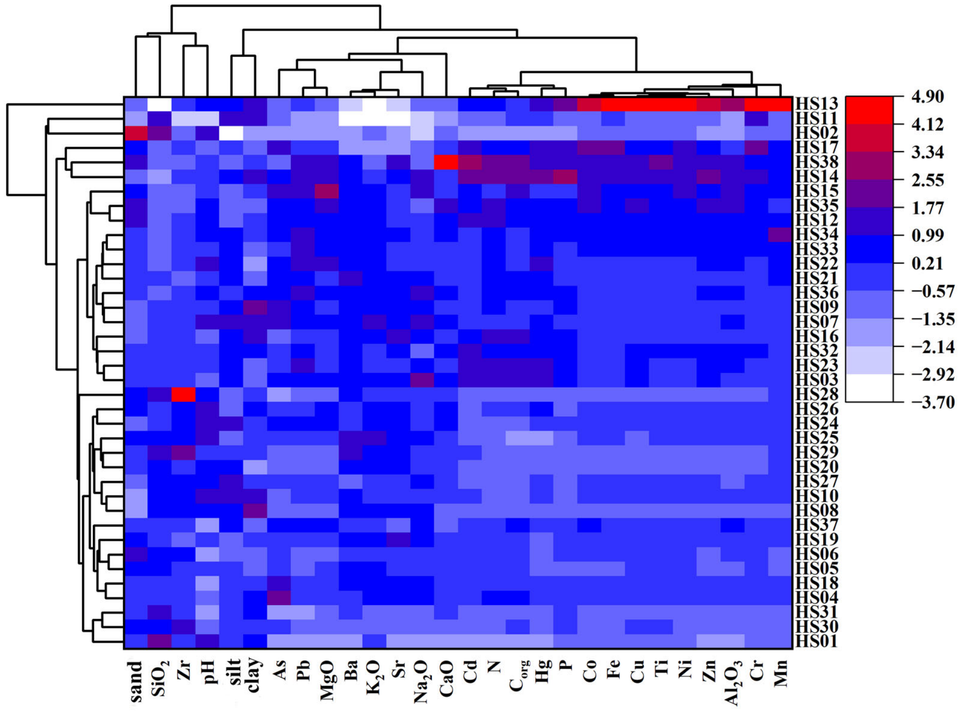


Figure 6. Clustered heat map of sediment trace and macronutrients.

The correlation analysis provided a preliminary prediction of the source using the strength of association that exists between the variables, and the cluster analysis corroborated the correlation analysis above while also assigning the different sources, which are represented as white to red in the spatial scale (Figure 6). The clustering heat map divided the variables into two major families. Family 1 included sand grains, SiO_2, and pH. Family 2 included powder grains, sticky grains, As, Pb, MgO, Ba, K_2O, Sr, Na_2O, CaO, Cd, N, Corg, Hg, P, Co, Fe, Cu, Ti, Ni, Zn, Al_2O_3, Cr, and Mn. Based on this, the dendrogram also divided family 2 into three subgroups: Group 1 contained silt and clay; Group 2 contained As, Pb, MgO, Ba, K_2O, Sr, Na_2O, and CaO; and Group 3 contained Cd, N, C_{org}, Hg, P, Co, Fe, Cu, Ti, Ni, Zn, Al_2O_3, Cr, and Mn. MgO, K_2O, CaO, and Na_2O may represent a mixture of terrestrial-sourced detritus, bioclastic detritus, and oceanic chemical- and volcanic-sourced material deposited. Previous studies have shown that Ba, Sr, and Pb are easily enriched in sediments rich in MgO, K_2O, CaO, and Na_2O. From the cluster analysis and the correlation analysis above, combined with the study of Yongo et al. [38], it can be hypothesized that the heavy metals As, Pb, Ba, and Sr are mainly related to biological effects and geological conditions, and therefore Group 2 was classified as a natural source. Combined with the clustering heat map and correlation description, the heavy metals contained in Group 3 should be mainly from industrial and agricultural composite sources. Around Dongzhai Harbor, there are economic development industries such as agricultural science and technology enterprises, fish breeding bases, fertilizer science and technology enterprises, and a shipping industry. The discharge of wastewater from agriculture and aquaculture, as well as oxidized and oily sewage discharge from ships, will also lead to the input of heavy metals to the wetland.

The correlations showed highly significant positive correlations between As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Ti, Zn, and Al_2O_3, indicating a correlation with terrestrial sources of detrital deposition. However, Cd, Co, Cr, Cu, Hg, Ni, Pb, Ti, Zn, and the nutrients N, P, and C_{org} also showed highly significant positive correlations with As, Mn, and the nutrients N, P, and C_{org}. Combined with the comparison of background values and Makokha et al. [39], it can be hypothesized that the sources of these 11 heavy metals should be a mixture of natural and anthropogenic. In addition, Ba, Cd, Hg, Pb, and Sr showed highly significant positive correlations with CaO; additionally, As, Ba, Pb, and Sr showed highly significant positive correlations with Na_2O and K_2O. Calcium is a characteristic element of marine-derived sediments and represents biogenic calcareous deposition, whereas Na_2O and K_2O mainly represent volcanic rock sources and marine chemical deposition. In summary, the sources of heavy metals in the mangrove wetland sediments of Dongzhai Harbor are more complicated, and the sources include a mixture of terrestrial clastic deposition, anthropogenic inputs, bioclastic deposition, volcanic rock material sources, and marine chemical deposition.

4.2. Contamination Status and Potential Ecological Risk

In this study, the sum of toxicity response factors was 106, so the corresponding RI limit value was adjusted ($150 \times 106/133 \approx 120$) [24]. The adjusted ecological risk evaluation level is shown in Table 4. In this study, the geochemical background values of Hainan Island released by the China Environmental Monitoring General Station in 1990 were used as the background values [26].

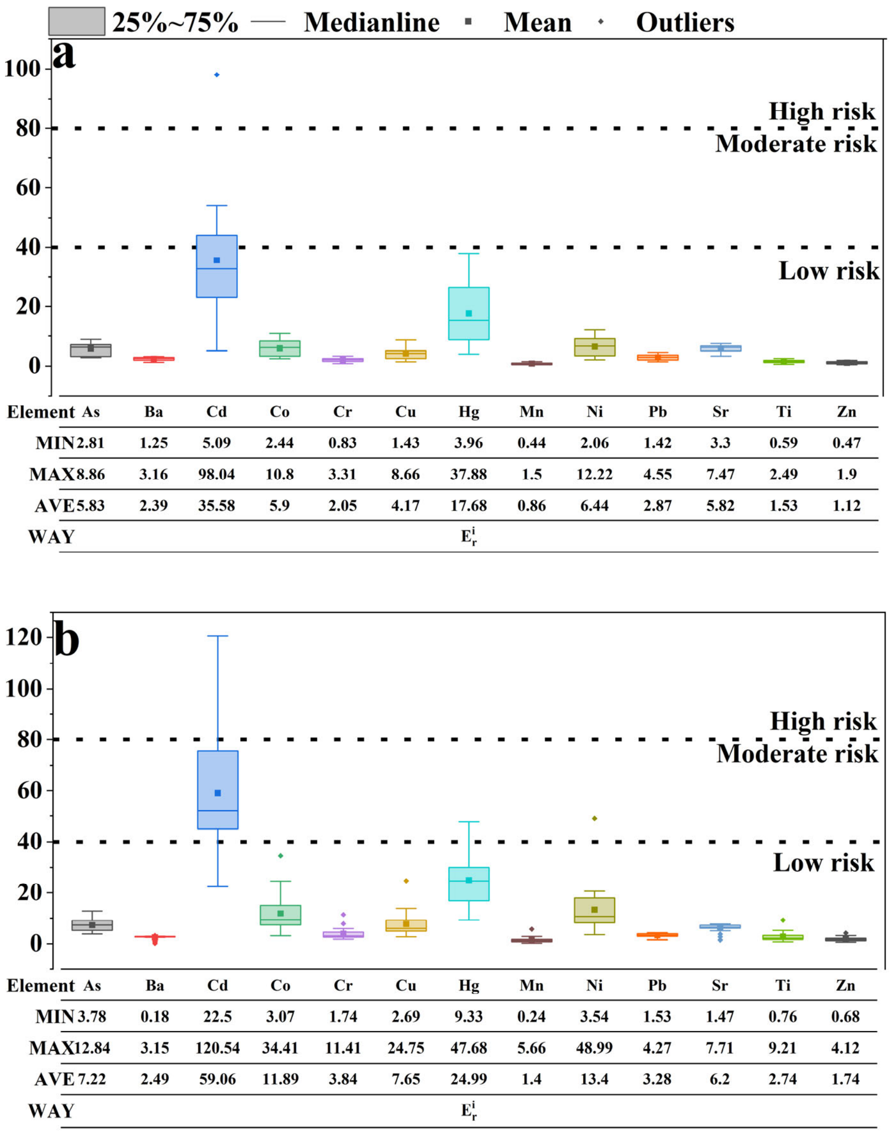
Table 4. Pollution factors, potential ecological risk factors and degree classification.

E_r^i	Level of Potential Ecological Risk	RI	Level of Potential Ecological Risk
$E_r^i < 40$	Low risk	RI < 120	Low risk
$40 \le E_r^i < 80$	Moderate risk	$120 \le RI < 240$	Moderate risk
$80 \le E_r^i < 160$	Heavy risk	$240 \le RI < 480$	Serious risk
$160 \le E_r^i < 320$	Serious risk	$RI \ge 480$	Extremely serious risk
$E_r^i \ge 320$	Extremely serious risk		

The potential ecological risk index (E_r^i) values of individual heavy metals in the surface sediments of the eastern part of Dongzhai Harbor wetland were, in descending order, Cd (35.58) > Hg (17.69) > Ni (6.44) > Co (5.9) > As (5.84) > Sr (5.82) > Cu (4.17) > Pb (2.87) > Ba (2.38) > Cr (2.05) > Ti (1.53) > Zn (1.12) > Mn (0.86) (Figure 7, Table 5). After risk-factor grading, all heavy metal elements in the eastern part of the wetland were at low risk levels overall (Table 4). However, from Table 5 Cd was at a medium-risk level (3 sampling points: HS22, HS29, and HS36) and a higher-risk level (1 sampling point, HS23) at some points. The source analysis above shows that Cd, mainly from agricultural sources, poses a certain ecological risk to the wetland ecosystem.

Table 5. Individual potential ecological risk index values for heavy metal elements in eastern and western wetland sediments.

	East			West		
Element	$E_r^i < 40$	$40 \le E_r^i < 80$	$80 \le E_r^i < 160$	$E_r^i < 40$	$40 \le E_r^i < 80$	$80 \le E_r^i < 160$
As	13	0	0	25	0	0
Ba	13	0	0	25	0	0
Cd	9	3	1	6	13	6
Co	13	0	0	25	0	0
Cr	13	0	0	25	0	0
Cu	13	0	0	25	0	0
Hg	13	0	0	24	1	0
Mn	13	0	0	25	0	0
Ni	13	0	0	24	1	0
Pb	13	0	0	25	0	0
Sr	13	0	0	25	0	0
Ti	13	0	0	25	0	0
Zn	13	0	0	25	0	0



Element	As	Ba	Cd	Co	Cr	Cu	Hg	Mn	Ni	Pb	Sr	Ti	Zn
MIN	2.81	1.25	5.09	2.44	0.83	1.43	3.96	0.44	2.06	1.42	3.3	0.59	0.47
MAX	8.86	3.16	98.04	10.8	3.31	8.66	37.88	1.5	12.22	4.55	7.47	2.49	1.9
AVE	5.83	2.39	35.58	5.9	2.05	4.17	17.68	0.86	6.44	2.87	5.82	1.53	1.12
WAY	E_r^i												

Element	As	Ba	Cd	Co	Cr	Cu	Hg	Mn	Ni	Pb	Sr	Ti	Zn
MIN	3.78	0.18	22.5	3.07	1.74	2.69	9.33	0.24	3.54	1.53	1.47	0.76	0.68
MAX	12.84	3.15	120.54	34.41	11.41	24.75	47.68	5.66	48.99	4.27	7.71	9.21	4.12
AVE	7.22	2.49	59.06	11.89	3.84	7.65	24.99	1.4	13.4	3.28	6.2	2.74	1.74
WAY	E_r^i												

Figure 7. (**a**) Individual potential ecological risk index (E_r^i) for heavy metals in sediments from the eastern part of the wetland, (**b**) individual potential ecological risk index (E_r^i) for heavy metals in sediments from the western part of the wetland.

The potential ecological risk index values of the various heavy metals in the surface sediments in the western part of the mangrove wetland of Dongzhai Harbor were, in descending order, Cd (59.06) > Hg (24.99) > Ni (13.4) > Co (11.89) > Cu (7.65) > As (7.22) > Sr (6.2) > Cr (3.84) > Pb (3.28) > Ti (2.74) > Ba (2.49) > Zn (1.74) > Mn (1.4). From the grading of potential ecological risk coefficients, most of the heavy metal elements in the western part of the wetland were at low risk levels, except for Cd, which exhibited a medium potential ecological risk level (Table 5, Figure 5). Table 5 further shows that Cd reached a medium risk level in 13 sampling sites in the west, accounting for 52% of the total sites, and 6 sampling sites reached a higher risk level (HS03, HS13, HS14, HS17, HS32, and HS38). The elements Hg and Ni also reached medium risk levels at individual points (1 sampling point each, HS14 and HS13, respectively). This was likely due to the high level of urbanization and agricultural activities in the vicinity [40] Therefore, extra attention needs to be paid to the levels of Cd, Hg, and Ni in the wetland to avoid health threats to the wetland's ecology.

4.3. Evaluation of the Nemero Index

The Nemero index evaluation (PN) was first proposed by Nemerow in 1974 [41], and it is one of the most used methods for comprehensive pollution index calculations at present. The Nemero pollution index has been applied to analyze the pollution status of sediments in the Shatt al-Arab basin by Allafta et al. [42]. The combined pollution index (PN) of heavy metal Nemero in the surface sediments of the eastern and western parts of the mangrove wetland in Dongzhai Harbor, Hainan, showed that the wetland was at a moderate level of pollution (Figure 8). The PN values in the eastern part of the wetland ranged from 1.2 to 2.78, with a mean value of 2.19. A total of 31% of the points were mildly contaminated, and these points were usually located in terrestrial areas near the coastline, which are away from human impacts and sparsely vegetated. In the eastern part of the wetland, 69% of the points were moderately polluted, and they were mostly located in the southeastern corner of the wetland, which belonged to the densely populated area, and the pollution was very likely to develop to the level of heavy pollution, so it is necessary to carry out detailed detection and prevention work in the future. The PN values in the western part of the wetland ranged from 2.13 to 7.38, with a mean value of 2.95, and the western part of the wetland had a higher level of pollution. Among them, 80% of the points showed moderate pollution, and 20% of the points were heavily polluted. These points were usually located near villages and towns and in areas with lush vegetation, which provide favorable conditions for the input and deposition of heavy metals, and, therefore, it is also necessary to carry out necessary monitoring and preventive work, so as not to cause ecological damage.

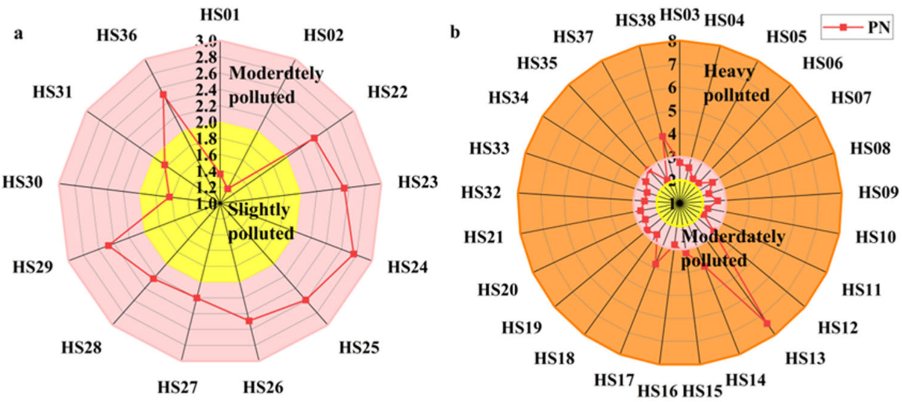


Figure 8. (**a**) Heavy metal Nemero index (PN) for sediments in the eastern part of the wetland, (**b**) heavy metal Nemero index (PN) for sediments in the western part of the wetland.

The analysis based on the potential ecological risk index method and the improved Nemero index method showed that the heavy metals exhibited significant ecological risks in the southeastern part of the Dongzhai Harbor wetland, as well as in the western part of the wetland. Geographically located in a densely populated area, and characterized by concentrated industrial and agricultural development, the pollution situation in the wetland showed a moderate-to-heavy pollution level. The main polluting elements in the wetland included Cd, Hg, and Ni, among which the ecological risk posed by Cd was high at some points. The discharge of industrial and agricultural wastewater should be strictly controlled in future pollution prevention and control work in combination with the evaluation and analysis related to biological toxicity.

5. Conclusions

In this paper, the mangrove wetland of Dongzhai Harbor in Hainan was selected as the study area, and the spatial distribution, source, and ecological risk of heavy metals in the wetland sediments were analyzed. The following main conclusions were obtained.

(1) In terms of spatial distribution, the contents of heavy metals in the western part of the wetland were significantly higher than those in the eastern part. The heavy metals Cd, Co, Cr, Cu, Hg, Mn, Ni, Zn, and Ti were mainly distributed in the area of human activities, and were greatly influenced by human activities. The heavy metals As, Pb, Ba, and Sr were distributed in significantly high levels in all locations except the northern part of the wetland, which might be more strongly influenced by natural factors such as physical sources and tides.
(2) The sources of heavy metals in the wetland sediments were categorized and resolved using correlation analysis and cluster analysis. It was concluded that As, Ba, Pb, and Sr mainly came from natural sources; Co, Cr, Cu, Mn, Ni, Ti, and Zn mainly came from industrial sources; and the input of heavy metals from agricultural sources mainly included Cd and Hg.
(3) The potential ecological risk index (RI) and the Nemero index (PN) pointed out that the main polluting elements of the wetland were Cd, Hg, and Ni, with agricultural sources as the main source of pollution; furthermore, there were obvious ecological risks of heavy metals in the western and southeastern corners of the wetland, which were in the inland area far away from the coastline, close to the range of human activities, and characterized by dense mangrove vegetation.

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