Heavy Metal Contamination of Urban Mangrove Sediments and Their Environmental Significance in the Zhanjiang Bay

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Abstract

Urban mangroves can be used to measure the impact of human activities on the urban ecological environment because mangroves are sensitive to human activities. However, studies on the evaluation of heavy metal elements in urban mangroves are still limited. Consequently, this study selected the urban mangroves in a central commercial area of Zhanjiang Bay as a case study to investigate the content and distribution of the heavy metal elements in mangrove sediments. Combined with the results of elemental analysis, grain size analysis, risk level, influencing factors, and sources of heavy metal pollution in the surficial sediments of the mangroves in the study area were evaluated based on mathematical models and multivariate statistical analysis. The results show that (1) concentration of heavy metals: $V > Pb > Cu > Ni > As > Co > Cd > Hg$; (2) the content of the eight heavy metal elements has a significant positive correlation with total organic carbon (TOC) and total nitrogen (TN) values, likely as a result of adsorption, complexation, or precipitation of heavy metals by organic matter in the sediments; (3) the mangrove sediments in the study area are affected by heavy metal pollution, among which Cd pollution is the heaviest, followed by Hg pollution; (4) comprehensive analyses of multiple heavy metals using Potential Ecological Risk Index shows that the risk level of the study area is slight to very strong ecological risk; (5) the heavy metals in the study area are mainly derived from human activities such as urban domestic sewage, transportation, and ship pollution.

1. Introduction

Mangrove is a woody plant community that grows in the coastal intertidal zone of the transitional area between land and sea. It is dominated by evergreen trees or shrubby mangrove plants. It plays an important role in preventing wind and waves, purification of seawater, and carbon sequestration and storage (Cheng Q et al., 2021). However, rapid urbanization, industrialization, and industrial and agricultural production activities in coastal areas in recent decades have generated a large number of heavy metal pollutants, which flow into the ocean along with surface runoff and directly discharge nearshore, causing serious destruction to mangroves (Jiang R et al., 2020; Feng Y et al., 2012; Sarker S et al., 2021). The mangrove wetland ecosystem has a strong interception, adsorption, and fixation effects on heavy metals due to its unique habitat characteristics, and thus it often becomes a pollution sink for heavy metal pollutants (Silva C et al., 2006; Kumar A et al., 2016; Soto-Jiménez M F Páez-Osuna F, 2001). Heavy metal pollutants have been a research focus for a large number of scholars in the world since the heavy metals have diverse sources, strong resistance to decomposition, long residual time, high toxicity, etc., and may even cause great harm to biological and human health through the food chain or other migration pathways (Nath B et al., 2013; Hu B et al., 2021). Up to now, numerous studies have been conducted on the pollution of heavy metals in mangrove ecosystems in diversified regions at home and abroad (Jiang R et al., 2020; Costa-Bdeder S et al., 2020; Shi C et al., 2019). However, previous research areas are principally concentrated in industrial areas and ecological protection areas, few studies have been carried out on heavy metal pollution of mangroves in the urban central business district. Therefore, this study selected the Zhanjiang Bay mangroves in the central business district of Zhanjiang City, Guangdong Province as the research object, covering the shortage of data for heavy metal pollution research.

Guangdong Zhanjiang Mangrove Nature Reserve is the largest natural distribution area of mangroves in mainland China (Li M S et al., 2013). With the speeding up of industrialization and urbanization in Zhanjiang City, aquaculture, industrial pollution, vessel pollution, and domestic pollution in the bay increase by years, resulting in a rapid accumulation of heavy metal pollutants in mangrove sediments, although the mangrove wetlands have a certain tolerance for heavy metal pollutants. As a result, the coastal mangrove wetland in Zhanjiang City has an increasingly severe environmental pressure (Xu S et al., 2015; Bo H et al., 2021). In this study, heavy metal content in 25 surficial sediment samples from Zhanjiang Bay mangroves in the central urban area of Zhanjiang City in South China has been measured through ICP-MS, elemental analysis, and grain size analysis, aimed at acquiring a better understanding of mangroves in a central urban area: (1) status and characteristics of heavy metal pollution; (2) comprehensive evaluation of ecological environment quality and

source-to-sink analysis of heavy metal pollutants; 3) to lay a theoretical foundation for pollution prevention and control, more specifically, for reasonable prevention and control of heavy metal pollution in mangrove wetland sediments.

2. Materials And Methods

2.1. Research Area

The studied mangrove forest is located on the northwest bank of Zhanjiang Port, back against the downtown area of Zhanjiang City. This area has a mild climate, fertile water, and abundant plankton. Jinshawan is subtropical with an average annual temperature of 24.1°C, which is well suitable for mangrove growth. This area is artificially planted mangroves, including *Sonneratia apetala*, *Kandelia candel*, and *Avicennia marina*, and it is close to the centre of Zhanjiang City (Fig. 1).

2.2. Sample collection and analysis

Mangrove sediment samples of Zhanjiang Bay were collected in January of 2020. 25 sampling stations from south to north along the mangrove distribution area were deployed (Fig. 1). The samples were collected in the surface sediment of 0-10 cm thick after clearing away the surface debris during sampling. Each sample was mixed up homogeneously before being sealed in a clean sample bag. Each soil sample is weighted about 1 kg. In total, 25 samples were collected. The collected soil is mainly muddy soil.

2.2.1. Measurement of heavy metal elements in mangrove sediments

The instrument used for the determination of trace elements is Varian 820 ICP-MS. Relevant parameters of analysis and determination are shown in Table 1. The experimental procedure is as follows: samples of 0.04 g were weighed accurately and put into a Teflon cup before adding 1.5 mL hydrofluoric acid and 0.5 ml nitric acid. The cup was then sealed and placed in an oven at 180°C for 12 h. Evaporation of acid was performed on an electric hot plate kept at 150°C after the cup was taken out from the oven and cooled down to room temperature. Similarly, the cup was again added with 1 mL nitric acid and 1 mL water before being sealed in the oven at 150 °C for 12 h. Finally, the cup was taken out and cooled down to room temperature. The samples were weighed and diluted to 40 g (at a dilution ratio of about 1000) for the determination of trace elements through ICP-MS.

2.2.2. Element analysis

Each sample of 0.5 g was put into the centrifuge tube and 5 mL hydrochloric acid was added for a chemical reaction of 8-12 h, during which it was mixed up 2-3 times on a vortex mixer. The supernatant was carefully sucked out with a dropper and 5 mL deionized water was added to wash the sample after the supernatant was centrifuged for 6 min (2000 r/min) and discarded. The above procedure was repeated 5-6 times until the pH value of the supernatant is about neutral. The acidified samples were freeze-dried in a vacuum for 48 h. All the dried samples were taken out, ground, and mixed, before being placed in a stainless steel crucible fired at 450°C, to keep dry and preserve for measurement. The organic carbon and nitrogen elements in the sediments were determined using the Elementar varioMAXCN elemental analyzer with an error of less than 5%.

2.2.3. Physical Parameters

pH values of sediment samples were determined using a glass electrode pH meter (E-201-L, pH composite electrode). A grain size analyzer (PSA, Coulter, model L 230) was used to measure the grain size of the surface sediments.

2.2.4. Statistical Analysis

Origin 2018 was applied to conduct descriptive statistical analysis on the heavy metal content of mangrove sediments in Zhanjiang Bay, and SPSS 26.0 was utilized to perform correlation analysis, principal component analysis, and cluster analysis on the heavy metal data of mangrove sediments. The KMO and Bartlett method was used to test the suitability of factor analysis on the original data set, followed by the principal component analysis. Origin 2018 was also used for drawing.

2.3. Evaluation Methods

2.3.1. Evaluation based on The Geological Accumulation Index

The Geological Accumulation Index method is a commonly used evaluation index for heavy metal pollution in sediments (Muller G et al., 1969). The formula is as follows:

$$I_{geo} = \log_2 \left[\frac{C_i}{k \times B_i} \right] \quad (1)$$

In the above formula, I_{geo} is the geological enrichment coefficient, C_i is the measured value of certain heavy metal i , and B_i is the geochemical background value of the heavy metal i in sedimentary rocks. In this formula, B_i was determined using the background value of soil inorganic elements in Guangdong Province during "The 7th Five-Year Plan" (Zhang S L et al., 2012). The degree of heavy metal pollution can be divided into 5 levels according to the classification of the I_{geo} values, with specific thresholds shown in Table 1.

Table 1 Application of The Geological Accumulation Index of heavy metals in sediment in identification/classification of pollution levels

I_{geo}	level	Pollution degree
$I_{geo} \leq 0$	0	nonpollution
$0 \leq I_{geo} \leq 1$	1	Mild pollution
$1 \leq I_{geo} \leq 2$	2	Moderate pollution
$2 \leq I_{geo} \leq 3$	3	Middle-level pollution
$3 \leq I_{geo} \leq 4$	4	Strong pollution
$I_{geo} \geq 4$	5	Extreme pollution

2.3.2. Evaluation on the basis of the Potential Ecological Risk Index

The Potential Ecological Risk Index has been applied in an evaluation method proposed by the famous Swedish geochemist Hakanson (1980) to evaluate the degree of heavy metal pollution. Its calculation formula is as follows (Hakanson L, 1980; Xu Z Q et al., 2008)

$$RI = \sum_{i=1}^m E_r^i = \sum_{i=1}^m T_r^i \times C_f^i = \sum_{i=1}^m T_r^i \times \frac{C_i}{C_n^i} \quad (2)$$

In the formula, m represents the type of pollutant and R_i is the Potential Ecological Risk Index of multiple heavy metals. R_i indicates the overall potential ecological risk degree. E_r^i is the Potential Ecological Risk Index of single heavy metal i , pointing to the ecological risk level of a single pollutant. T_r^i is the response factor of the heavy metal toxicity coefficient. Specifically, the toxicity response coefficients of Co, V, Cu, Pb, Ni, As, Cd, and Hg are 5, 2, 5, 5, 5, 10, 30, and 40, respectively. C_f^i is the pollution parameter of pollutant i , representing heavy metal content measured in this study. C_n^i is the reference value of heavy metal i . The criteria for the classification of potential ecological risks in accordance with the size of E_r^i and R_i is shown in Table 2:

Table 2 Potential Ecological Risk Index and risk levels

E_r^i	Potential ecological risk degree	R_i	Overall potential ecological risk degree
$E_r^i < 40$	Slight	$R_i < 150$	Slight
$40 \leq E_r^i < 80$	Medium	$150 \leq R_i < 300$	Medium
$80 \leq E_r^i < 160$	Strong	$300 \leq R_i < 600$	Strong
$160 \leq E_r^i < 320$	Very strong	$R_i \geq 600$	Very strong
$E_r^i \geq 320$	Fortissimo		

3. Results

3.1. Statistical analysis of the basic physical and chemical properties of mangrove sediments in the study area

The variation of sand, silt, and clay in the mechanical composition of mangrove sediments in Zhanjiang Bay are relatively small. The TOC and TN values of mangrove sediments have large variation coefficients, and the pH value is weakly acidic. The physical and chemical conditions of the sediments are shown in Table 3. The variation coefficients of pH, sand, silt, and clay are 0.05, 0.33, 0.40, and 0.39, respectively, with an overall small variation. The content of sand in the mechanical composition of mangrove sediments is relatively high in the study area, followed by silt, as indicated by the mean value of grain size. The coefficient of variation of gravel, TOC, and TN values is relatively high, showing that the TOC, TN, and gravel values of the mangrove sediments have a significant spatial discrepancy.

In general, sediments in the urban mangrove wetland of Zhanjiang Bay in Zhanjiang City are weakly acidic, with a pH value between 6.21 and 7.41 and a mean value of 6.67. The contents of TOC and TN in the mangrove sediment are in the range of 0.14-4.94% and 0.02-0.65%, respectively, with mean values of 1.24% and 0.13%, respectively. Samples with the maximum TOC and TN values are present in sampling station JSW10 at the sewage outfall (Fig. 1) and their contents significant difference of the TOC and TN content exists in spatial distribution. High TOC and TN content at the sewage outfall may be caused by strong decomposition and accumulation of litter in the sediments at the sewage outfall where domestic sewage discharge is high and hydraulic action is weak.

Table 3 Statistics of physical and chemical properties of mangrove sediments in the study area

Physical and chemical indicators	Minimum	Maximum	Mean	Standard deviation	Coefficient of variation
pH	6.21	7.41	6.67	0.34	0.05
TOC(%)	0.14	4.94	1.24	1.24	0.81
TN (%)	0.02	0.65	0.13	0.13	1
Gravel grain size (%)	0.00	22.8	1.15	4.50	3.91
Sand grain size (%)	20.44	79.75	54.86	16.77	0.31
Silt particle size (%)	15.29	62.75	36.18	13.98	0.39
Clay grain size (%)	2.46	17.47	8.72	3.34	0.38

Note (Wu K N and Zhao R, 2019): gravel grain size (> 2 mm), sand grain size (0.02-2 mm), silt grain size (0.002-0.02 mm), and clay grain size (<0.002 mm)

3.2. Descriptive statistics of heavy metal content

According to the statistical results of soil background value survey, the background values of heavy metal elements in the soil of Guangdong Province are Co=7.0 mg/kg, V=65.3 mg/kg, Cu=17 mg/kg, Pb=36 mg/kg, Ni=14.4 mg/kg, As=8.9 mg/kg, Cd=0.056 mg/kg, and Hg=0.078 mg/kg, respectively. Content of heavy metals in urban mangrove sediments in the study area is shown in Fig. 2, suggesting an relationship of V > Pb > Cu > Ni > As > Co > Cd > Hg. Content of Co is in the range of 1.33 to 6.65 mg/kg, averaging 2.91 mg/kg, within the extent of soil background value in Guangdong Province. Content of V is in the range of 11.92 to 87.71 mg/kg, averaging 29.96 mg/kg. 4% of the samples have a higher content of V than that of the soil background value in Guangdong Province, with the maximum times of 1.3 out of limits. Content of Cu is in the range of 4.05 to 58.95 mg/kg, averaging 18.24 mg/kg. Cu content of samples in 40% of all the sample sites exceeds that of the soil background value of Guangdong Province, with the maximum times of 3.47 out of limits. The highest Cu content exists in JSW10, located at the sewage outfall. Content of Pb is in the range of 9.95 to 42.67 mg/kg, averaging 20.07 mg/kg. 8% of the samples have a higher Pb content exceeding that of the soil background value in Guangdong Province, with the maximum times of 1.18 out of limits. Content of Ni is in the range of 2.96 to 21.88 mg/kg, averaging 7.86 mg/kg. Ni content of samples in 16% of all the sample points exceeds that of the soil background value in Guangdong Province with the maximum times of 1.52 out of limits. Content of As is in the range of 2.31 to 11.23 mg/kg, averaging 5.0 mg/kg. 8% of all the samples have a higher As content than that of the background value in Guangdong Province, with the maximum times of 1.26 out of limits. Content of Cd is in the range of 0.06 to 0.42 mg/kg averaging 0.19 mg/kg. Cd content of sediments from all the sample stations is higher than that of the soil background value in Guangdong Province, with a maximum multiple of 7.5 times at the sampling station of JSW10 located at the sewage outfall. Content of Hg is in the range of 0.03 to 0.58 mg/kg, averaging 0.09 mg/kg. 32% of the samples have a higher Hg content than that of the soil background value in Guangdong Province and the maximum multiple is 7.4 times. The highest content of Hg is present in sample station JSW10, located at the sewage outlet. Collectively, a certain degree of heavy metal pollution exists in the mangrove sediments of the study area.

4. Discussion

4.1. Correlation between physical and chemical properties of mangrove sediments and content of heavy metals

The accumulation and distribution of heavy metals in mangrove sediments are affected by factors such as the tidal characteristics of the sea area where they are located, the content of organic matter, the physical and chemical properties of the sediments, and the biological processes of the mangroves (Shi C et al., 2019; Silva C et al., 2006; Sun X et al., 2020).

The Pearson correlation analysis was carried out between heavy metal elements in the sediments and TN, TOC, grain size, and pH values, in order to study the relationship between the heavy metal content in mangrove sediments at the Sea Viewing Corridor and its environmental controlling factors. The results show that a significant positive correlation is present between the content of the 8 heavy metals and the contents of TOC and TN (Table 4). Organic matter has strong adsorption properties for heavy metals through adsorption, complexation, and precipitation effects, as a result of surface adsorption, cation exchange, and chelation reaction. The accumulation of organic matter makes it much easier for sediments to adsorb heavy metals (Yang X et al., 2010; Lasota J et al., 2020). Previous studies have shown that TOC and TN play an important role in the absorption and chelation of heavy metals (Contreras S et al., 2018). The content of Hg in the surficial sediments of mangroves has a significant positive correlation with the pH value. pH affects the solubility, redox, deposition and dissolution, adsorption and desorption, and other processes of Hg in sediments, as well as a microbial modification on Hg in the sediments (Ding Z H et al., 2009). seven heavy metals, excluding Cu, have a significant negative correlation with sand grains and a significant positive correlation with silt grains. Five heavy metals, except for Cu and Cd, have a significant positive correlation with clay. Previous studies have proposed that sediment grain with small grain size and a large surface area generally absorb more heavy metals. Coarse-grained substances have a diluting effect on concentrations of most metals. A significant negative correlation exists between sand and heavy metal content, as shown by an increase of the content of heavy metals with the decrease of grain size. However, the concentration of all heavy metals does not necessarily increase with the decrease in grain size of the sediment. For example, the concentration of heavy metals Co, V, and Cd in the sediment is higher in sediments with grain size larger than 63 μm (Vosoogh A et al., 2017; Soto-Jiménez M F and Páez-Osuna F 2001).

Table 4 Correlation of toxic metal elements with grain size, TOC, TN and pH values

Metal element	gravel grain size $>2\text{ mm}$	Sand grain size $0.02\text{--}2\text{ mm}$	Silt grain size $0.002\text{--}0.02\text{ mm}$	Clay grain size $<0.002\text{ mm}$	TOC%	TN%	pH
Co	-0.287	-0.859**	0.848**	0.835**	0.863**	0.779**	0.091
V	-0.247	-0.895**	0.873**	0.903**	0.852**	0.723**	-0.123
Cu	0.105	-0.358	0.343	0.244	0.570**	0.652**	0.377
Pb	0.220	-0.897**	0.881**	0.884**	0.911**	0.827**	0.007
Ni	0.197	-0.882**	0.865**	0.869**	0.931**	0.855**	0.055
As	0.227	-0.807**	0.784**	0.846**	0.691**	0.522**	-0.183
Cd	0.086	-0.623**	0.627**	0.491*	0.824**	0.924**	0.437*
Hg	0.008	-0.510**	0.521**	0.400**	0.723**	0.866**	0.548**

Note: ** Correlation is significant at percentile level.

4.2. Comparison between heavy metal content in this study and other studies at home and abroad

The content of heavy metals of Cu, Cd, and Hg in surface mangrove sediments in the study area is higher than that of the background value of soil elements in Guangdong Province (Table 5), indicating a certain degree of anthropogenic/man-made pollution. Table 5 shows a comparison of the heavy metal concentration of mangrove sediments in Zhanjiang Bay and that of other mangrove sediments in the world. The average content of Cu in the mangrove sediments of Zhanjiang Bay is 18.24mg/kg, which is higher than that of Donghai Island, Zhanjiang, Beihai of Guangxi, Senegal of West Africa, and Gulf of Khambh in India. Meanwhile, the average content of Pb is 20.07mg/kg, which is higher than that of Beihai of Guangxi, Senegal of WestAfrica, Gulf of Khambh in India, and Saudi Arabia. This may be explained by the location of

mangrove forests in Zhanjiang Bay, where the central business district of Zhanjiang City may generate a great number of pollutants. The surrounding dense population, well-developed traffic, high traffic volume, automobile exhaust emissions, and vehicle tire wear and tear may produce a large number of harmful gases and dust containing Cu, Cd, and Pb (Jeong H, and Ra K, 2021; Li H et al., 2015). The average content of heavy metal Cd is 0.19mg/kg, which is higher than that of Donghai Island in Zhanjiang, SouthernVietnam, Senegal in WestAfrica, Gulf of Khambh in India, The average content of heavy metal Hg is 0.09mg/kg, which is higher than that of Donghai Island in Zhanjiang and Guangxi Beihai. The content of Cd and Hg at the sewage outfall is much higher than that in other areas, so it is speculated that the pollution of Cd and Hg may have been derived from domestic sewage and transportation, as recreational parks and residential areas are constructed around the study area. In comparison with heavy metal pollution of mangrove surface sediments in other areas, the content of heavy metals in Zhanjiang Bay is generally moderate.

Table 5 Comparison of heavy metal content in surface sediments of domestic and international mangroves

Study Area	mg/kg								reference
	Co	V	Cu	Pb	Ni	As	Cd	Hg	
Zhanjiang Bay, Zhanjiang City	2.91	29.96	18.24	20.07	7.86	5.00	0.19	0.09	This study
Donghai Island, Zhanjiang City	-	-	12.50	27.00	17.20	12.50	0.04	0.07	(Luo S Y et al., 2018)
Dongzhai harbor, Hainan, China	-	-	19.51	20.52	30.40	8.52	0.56	-	(Wang J G et al., 2018)
Maowei sea Guangxi, China	20.10	-	61.90	48.90	50.70	-	0.79	-	(Jiang R et al., 2020)
Beihai of Guangxi, China	-	-	3.00	7.00	<3.00	3.00	-	0.04	(Vane C H et al., 2009)
Nansha, South China Sea	-	-	113.00	55.3	48.40	-	0.78	-	(Wu Q et al., 2014)
Futian of Shenzhen City, China	-	-	82.60	105.00	117.00	-	5.70	-	(Chai M et al., 2019)
Qi'ao Island, Zhuhai City, China	-	-	81.50	70.60	50.40	-	9.50	-	(Gopalakrishnan G et al., 2020)
Southern Vietnam	19.60	-	27.00	21.00	53.00	-	0.10		(Costa-Boeddeker S et al., 2017)
Senegal, WestAfrica	0.90	14.30	3.50	2.40	2.50	-	0.03	0.01	(Bodin N et al., 2013)
Gulf of Khambh, India	0.25	-	11.64	7.14	34.66	2.80	0.09	0.12	(Singh J K et al., 2020)
Saudi Arabia	3.94	759.15	209.80	4.40	81.05	23.75	1.67	1.98	(Al-Kahtany K et al., 2018)

Note“-” represents no data

4.3 Environmental risk assessment of heavy metal elements

4.3.1. Geological accumulation index

As shown in Table 6, the I_{geo} values of Co, V, Pb, and As in the 25 mangrove sediments collected from the sampling stations are all ≤ 0 , indicating that Co, V, Pb, and As are not polluted or weakly polluted. The pollution level of Cu is between unpollution and medium pollution. 80% of the sampling stations are unpolluted, 16% of the sampling stations are lightly polluted in Cu, and 4% of the sampling stations are moderately polluted in Cu. The pollution level of Ni ranges from unpollution to mild pollution in the mangrove sediments in Zhanjiang Bay, among which 96% of the sampling stations are unpolluted and 4% of the sampling points are mildly polluted. Cd pollution level is between unpollution and strong pollution in this study. 20% of the sampling stations are unpolluted, 44% of the sampling stations are mildly polluted, 20% of the sampling stations are partially moderately polluted, and 12% of the sampling stations are moderately polluted. Pollution, 4% of the sampling points are severely polluted. The pollution level of Hg is between unpollution and medium pollution in mangrove sediments in Zhanjiang Bay, among which 84% of the sampling stations are unpolluted, 8% are mildly polluted, 4% are partially moderately polluted, and another 4% are moderately polluted. Collectively, these result shows that Cu, Ni, Cd, and Hg pollutions exist in the mangrove sediments in Jinshawan, with the heaviest pollution of Cd, and followed by Hg.

Table 6 Geological Accumulation Index of heavy metals in mangrove sediments of the study area

I_{geo}	Grade	Proportion of heavy metals in mangrove sediments(%)							
		Co	V	Cu	Pb	Ni	As	Cd	Hg
≤ 0	nonpollution	100	100	80	100	96	100	20	84
[0,1]	Mild pollution	-	-	16	-	4	-	44	8
[1,2]	Moderate pollution	-	-	4	-	-	-	20	4
[2,3]	Middle-level pollution	-	-	-	-	-	-	12	4
[3,4]	Strong pollution	-	-	-	-	-	-	4	-
≥ 4	Extreme pollution	-	-	-	-	-	-	-	-

Note :“-” not detected

4.3.2. Potential ecological risk assessment

The potential ecological risk assessment of different heavy metals in the surface sediments of the mangrove wetland in Zhanjiang Bay are listed in Table 7. The potential ecological risks of the eight heavy metals in the sediments are in the order of $Cd > Hg > As > Cu > Pb > Ni > Co > V$. The Potential Ecological Risk Index of Cd is between 30.68 to 541.07, in the ecological hazard level of slight-extremely strong. The Potential Ecological Risk Index of Hg is between 15.38 to 297.44, suggesting an ecological risk level of mild to very strong. The Potential Ecological Risk Indexes of As, Cu, Pb, Ni, Co, and V are in the range of 2.60 to 12.62, 1.19 to 17.34, 1.38 to 5.93, 1.03 to 7.60, 0.95 to 4.75, and 0.37 to 2.69, respectively, showing their ecological risk levels are slight. In general, Cd has the highest level of potential ecological risk in mangrove sediments, followed by Hg. Overall, the Potential Ecological Risk Index value of Zhanjiang Bay mangrove wetland ranges from 53.58 to 889.44, based on comprehensive Potential Ecological Risk Indexes of multiple heavy metals. The comprehensive ecological risk level is slight-very strong. The evaluation results based on the Geological Accumulation Index method and the Potential Ecological Risk Index method are relatively consistent. Both of the evaluation results show that Cd and Hg are the predominated pollutants of mangrove sediments in the study area.

Table 7 Potential Ecological Risk Index of heavy metals in the study area

	E_r^i								<i>RI</i>
	Co	V	Cu	Pb	Ni	As	Cd	Hg	
Max	4.75	2.69	17.34	5.93	7.60	12.62	541.07	297.44	889.44
Minimum	0.95	0.37	1.19	1.38	1.03	2.60	30.68	15.38	53.58
Mean	2.08	0.92	5.37	2.79	2.73	5.61	104.36	44.72	168.58

4.4 Source to sink of heavy metals in the mangrove sediments

4.4.1. Correlation analysis

The correlation between heavy metals reveals whether they have homology, as heavy metals with a strong correlation may have the same source whereas heavy metals with weak correlation may have multiple sources (Zhang C et al., 2020). The Co-Pb-Cr-Ni-Cd, V-Pb-Ni-As, Cd-Hg-Ni-Pb in mangrove sediments of the study area have significant positive correlations, suggesting the same or a similar source (Table 8).

Table 8 Correlation between heavy metals in mangrove sediments

Metal element	Co	V	Cu	Pb	Ni	As	Cd	Hg
Co	1							
V	0.939**	1						
Cu	0.436*	0.341	1					
Pb	0.960**	0.964**	0.482*	1				
Ni	0.959**	0.951**	0.507**	0.988**	1			
As	0.839**	0.937**	0.139	0.872**	0.828**	1		
Cd	0.668**	0.556**	0.801**	0.694**	0.734**	0.330	1	
Hg	0.535**	0.408*	0.704**	0.565**	0.606**	0.196	0.947**	1

Note: ** Correlation is significant at percentile level.

4.4.2. Principal component analysis (PCA) and cluster analysis

Bartlett's sphericity test ($0.000 < 0.001$) and KMO measurement value test ($0.739 > 0.5$) were performed on mangrove sediment samples, The correlation analysis results show a strong positive correlation between all the elements (Table 8), indicating that data in this study is suitable for principal component analysis. The results of PCA are shown in Table 9. Two principal components with eigenvalues greater than 1 are obtained after performing Varimax orthogonal rotation on the Kaiser standardized factors. The contribution rates are 74.3% and 20.2%, respectively, with a cumulative contribution rate of 94.5%. These can be used to reveal most of the information about heavy metals. The contribution rate of the first principal component (F1), valued at 74.3%, is much higher than that of other principal components. The heavy metals Co, V, Cu, Pb, Ni, As, Cd, and Hg have higher loads. A strong or extremely strong positive correlation among the heavy metals suggests the above heavy metals may have the same or similar sources. The contribution rate of the second principal component (F2) is 20.2%. The heavy metals with higher load are Cu, Cd and Hg, suggesting that they may have the same

or similar origin. In addition, the cluster analysis results show that the heavy metals in Zhanjiang Bay mangrove sediments can be divided into three categories, with the first category of Pb, Ni, Co, V, and As, the second category of Cd, Hg, and the third category of Cu (Fig. 3). This is inconsistent with the results of principal component analysis.

The study area, located in the central business district of Zhanjiang City, has a dense population and a large traffic volume, as a result from adjacent to Zhanjiang Port, Xiashan Port, and many residential communities. Therefore, heavy metal pollution including Cu, Cd, and Pb may have been originated from traffic pollution such as automobile exhaust emission, tire wear, and ship pollution, while pollution in As from exhaust gas emission from coal combustion (Sodango T H et al., 2018). In addition, other studies have proposed that the heavy metals Ni and As in the soil of Guangdong Province are mainly related to the parent material of soil and geological affection rather than human activities (Chen Y L et al., 2019). The sewage outfalls in the mangrove forests of Zhanjiang Bay provide a large amount of urban production and domestic sewage discharged into the mangrove, increasing the content of heavy metal elements, such as Cd and Hg. Cd, Co, V, Cu, Pb, and other heavy metals in the urban mangroves of Zhanjiang Bay may have been mainly derived from urban transportation, urban sewage discharge, and ship pollution since the highest content of Cu, Cd, and Hg present in the sample station of JSW10 in the study area. The heavy metals Ni and As may have been principally originated from fossil fuel combustion and under influence of soil parent materials. The heavy metals Hg may have been dominantly from the discharge of urban domestic sewage. In summary, the heavy metals in the study area have been mainly affected by human activities such as urban domestic sewage, transportation, and ship pollution.

Table 9 principal component analysis matrix of heavy metals in mangrove sediments

Component	Heavy metal								Initial eigenvalue	Variation contribution/%
	Co	V	Cu	Pb	Ni	As	Cd	Hg		
F1	0.940	0.902	0.629	0.966	0.973	0.759	0.849	0.740	7.428	74.283
F2	-0.252	-0.412	0.588	-0.234	-0.178	-0.610	0.512	0.612	2.020	20.198

5. Conclusion

(1) Determination of content of heavy metals Co, V, Cu, Pb, Ni, As, Cd, and Hg in the mangrove surface sediments of Zhanjiang Bay show the average mass fractions are 2.91 mg/kg, 29.96 mg/kg, 18.24 mg/kg, 20.07 mg/kg, 7.86 mg/kg, 5.0 mg/kg, 0.19 mg/kg, and 0.09 mg/kg. The contents of Cu, Cd, and Hg are higher than those of the background values of soil elements in Guangdong Province.

(2) Contents of the 8 heavy metals studied have a significant positive correlation with the contents of TOC and TN. This may be explained by the reaction between the heavy metals and organic matter through surface adsorption, cation exchange, and chelation reactions, resulting in adsorption, complexation, and precipitation. As a result, the accumulation of organic carbon enhances the adsorption of heavy metals and the deposition of organic matter increases the accumulation of heavy metals. Seven heavy metals, excluding Cu, have a significant negative correlation with sand grains, whereas a significant positive correlation with silt grains. Six heavy metals, not including Cu and Cd, have a significant positive correlation with clay. The specific surface area increases as the grain size of sediments decreases, leading to an increase of the binding capacity with heavy metals, and thus an increasing content of heavy metals. This may be attributed to the different mineral composition, structure, and surface characteristics of sediments of different sizes.

(3) Overall, a certain degree of heavy metal pollution exists in surface sediments of the mangrove forests in Zhanjiang Bay, with the heaviest pollution of Cd, followed by Hg. Further research needs to be strengthened in the future. Specifically, detailed tests and investigations on the occurrence of forms, organic matter, and grain size of Cd and Hg are needed to be

carried out, in order to find out the enrichment mechanism and sources of Cd and Hg and provide theoretical support for the mangrove ecosystem protection as well as local Cd and Hg pollution prevention and control.

Declarations

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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Figures

Figure 1

Study area and sampling sites

Figure 2

Content of heavy metals in the study area

Figure 3

Cluster analysis of heavy metal