Research Article

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Characterization and ecological risk assessment of toxic metals in mangrove sediments near Langen Village in Tieshan Bay of Beibu Gulf, China

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Abstract: A series of coastal development initiatives have been recently implemented in the East Harbor area of Tieshan Harbor, Guangxi Province, China. However, the ecological impacts of these reclamation activities on toxic metal pollution levels in shallow mangrove sediments within the intertidal zones adjacent to Langen Village, Tieshan Bay (Beibu Gulf), remain poorly understood. This study investigated the distribution patterns, ecological risks, and potential sources of seven toxic metals (Pb, Cu, Zn, As, Cr, Cd, and Hg) in surface sediments collected from 26 sampling locations across dead mangrove zones, severely degraded mangrove areas, and currently intact mangrove ecosystems near Langen Village during April 2022. We employed multiple assessment metrics including the pollution load index (PLI), geoaccumulation index (I_{geo}), sediment quality guidelines, individual potential ecological risk factors, and potential ecological risk index (RI) to evaluate contamination status and associated ecological hazards. Results indicate moderate contamination and medium ecological risk according to I_{geo}, PLI and RI in intertidal sediments, with significantly higher toxic metal concentrations in dead and severely degraded mangroves than in temporarily undamaged areas. Total unit toxic index analysis revealed generally low biological toxicity from surface sediment metals, with Hg, Cd, and As identified as dominant ecological hazard factors. These findings provide a critical scientific basis for enhancing mangrove conservation strategies and developing targeted management protocols.

Keywords: mangrove forests, surface sediments, toxic metals, ecological risk assessment, Beibu Gulf, Langen Village

1 Introduction

Mangrove forests represent a distinct ecosystem that is found within the intertidal zones of temperate, tropical, and subtropical coastlines [1], recognized as one of the highest ecological service functioning natural systems on earth. They provide irreplaceable ecological services, including biodiversity maintenance, habitat provision, coastal protection, tidal erosion mitigation, and disaster resilience against tsunamis and hurricanes [2–4]. Additionally, they serve a crucial global function in carbon sequestration and storage, and are therefore categorized as blue carbon ecosystems [5].

Current environmental pressures from rapid coastal urbanization and industrial development have intensified pollutant emissions, exacerbating anthropogenic disturbances and degradation of mangrove ecosystems [6,7]. Mangrove wetland ecosystems are susceptible to substantial input of toxic metal pollutants, which are transported by tidal actions and surface runoff. This vulnerability arises from the combined effects of anthropogenic activities on land and the hydrodynamic and environmental conditions present in marine environments [8]. Mangrove sediments exhibit superior metal sequestration capacity due to their reducing conditions and sulfur-rich substrates, effectively trapping metals from water columns and suspended particulates,

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creating hotspots for toxic metal accumulation [9,10]. Since toxic metals are characterized by persistent, insidious, biotoxic, and non-degradable pollution, they will produce bioaccumulation effects through the role of the food chain, and therefore when metal concentrations exceed phytotoxic thresholds in mangrove tissues, they can induce physiological stress that disrupts ecosystem functioning and species composition, ultimately leading to ecosystem degradation [11].

Tieshan Harbor, a semi-enclosed natural deep-water harbor situated in Hepu County, Beihai City, Guangxi Province (northeastern Beibu Gulf), sustains abundant mangrove resources. However, recent port construction and land reclamation, coupled with anthropogenic pressures from aquaculture, maritime operations, port logistics, and emerging marine industries [12], have substantially modified the hydrodynamic regime, manifesting as diminished sediment flushing, attenuated tidal currents, and compromised aqueous self-purification capacity. These changes have precipitated mangrove habitat degradation and structural/functional decline throughout Tieshan Bay's ecosystems. Notably, intertidal mangroves near Langen Village (eastern Tieshan Harbor, Beibu Gulf) have displayed deterioration and mortality symptoms since 2017 following coastal development projects, with the affected area expanding annually and causing substantial ecosystem degradation [13]. Studies demonstrate that toxic metal pollution levels and associated ecological risks in northern coastal mangrove wetlands strongly influenced by adjacent terrestrial inputs have risen markedly over recent decades [14,15]. Consequently, investigating the influence of coastal engineering on toxic metal dynamics in Langen Village's mangrove sediments (Tieshan Bay, Beibu Gulf) is imperative for ecological preservation.

The objectives of the present study are to (1) analyze the distribution of Cu, Pb, Zn, As, Cd, Cr, and Hg in the surface sediments of mangrove ecosystems; (2) assess the level of pollution and potential ecological hazards using geoaccumulation index (I_{geo}), pollution load index (PLI), potential ecological hazard index (RI), and total unit toxic index (ΣTU); and (3) trace the possible sources of toxic metals through principal component analysis (PCA), hierarchical cluster analysis (HCA), and Pearson correlation analysis. These findings may establish a solid scientific foundation for the development and utilization of marine areas within Tieshan Harbor Bay as well as for the ecological preservation and restoration of mangrove forests.

2 Methods and materials

2.1 Study area

Tieshan Harbor is located along the eastern coast of the Beibu Gulf in Guangxi, characterized by a subtropical oceanic monsoon climate with a mean annual temperature of 23.0°C. According to the remote sensing monitoring and field survey data carried out by the Guangxi Mangrove Research Center (2019), the mangrove forest area in Tieshan Harbor Bay was 1108.69 hm^2, constituting 11.88% of Guangxi's total mangrove coverage [16]. Spatial distribution analysis revealed 27.42 hm^2 on the western coast and 485.48 hm^2 on the eastern coast [17]. These mangroves predominantly occupy intertidal zones spanning upper high-tide to lower mid-tide elevations, remaining submerged except during low-tide exposure. The most common mangrove forest species in Tieshan Harbor is *Avicennia marina*, and Tieshan Harbor is currently the largest natural *A. marina* growth area in China [16].

The largest mangrove standing along Tieshan Harbor's eastern shore is concentrated in the intertidal zone near Langen Village, Baisha Town, Hepu County, Beihai City. Chronic stressors including anthropogenic disturbances, pest infestations, and *Spartina alterniflora* invasion have degraded mangrove health and heightened ecosystem vulnerability. Since 2012, the East Harbor reclamation project has triggered severe habitat degradation and mortality in adjacent mangroves. By 2020, mortality zones spanned 17.18 hm^2 [17], predominantly as fragmented patches along tidal creeks. Dead mangroves exhibited calcified encrustations on stems, pneumatophores, branches, and foliage, indicative of prolonged physiological stress.

2.2 Sediment sample collection

Based on mangrove growth patterns along the nearshore zone of Langen Village (eastern Tieshan Harbor), three degradation categories were delineated: dead mangrove forest area (s1, s3, s4, s5, s6, s7, s11, s17, s21), severely degraded mangrove forest area (s2, s8, s9, s12, s14, s15, s16, s18, s19, s20, s22), and temporarily undamaged mangrove forest area (s10, s13, s23, s24, s25, s26) (Figure 1). Surface sediment sampling was carried out at a depth of 0–20 cm across 26 designated locations in April 2022 using a 0.025 m^2 Petersen grab sampler during low tide. During the sampling process, all living organisms, roots, litter, and any remnants of deceased biological material, as well as debris and detritus were meticulously removed. All samples of sediment were stored in clean polyethylene bags and recorded with latitude, longitude, and number of the sample point, then placed in a refrigerated container for transportation to the laboratory. After a 2-week drying period at room temperature, all soil samples were subjected to a 2 mm sieve to remove small gravel and larger debris. For the following chemical and physical analyses, the soil samples were finely ground to pass through nylon sieves with mesh sizes of 0.85 and 0.149 mm, respectively.

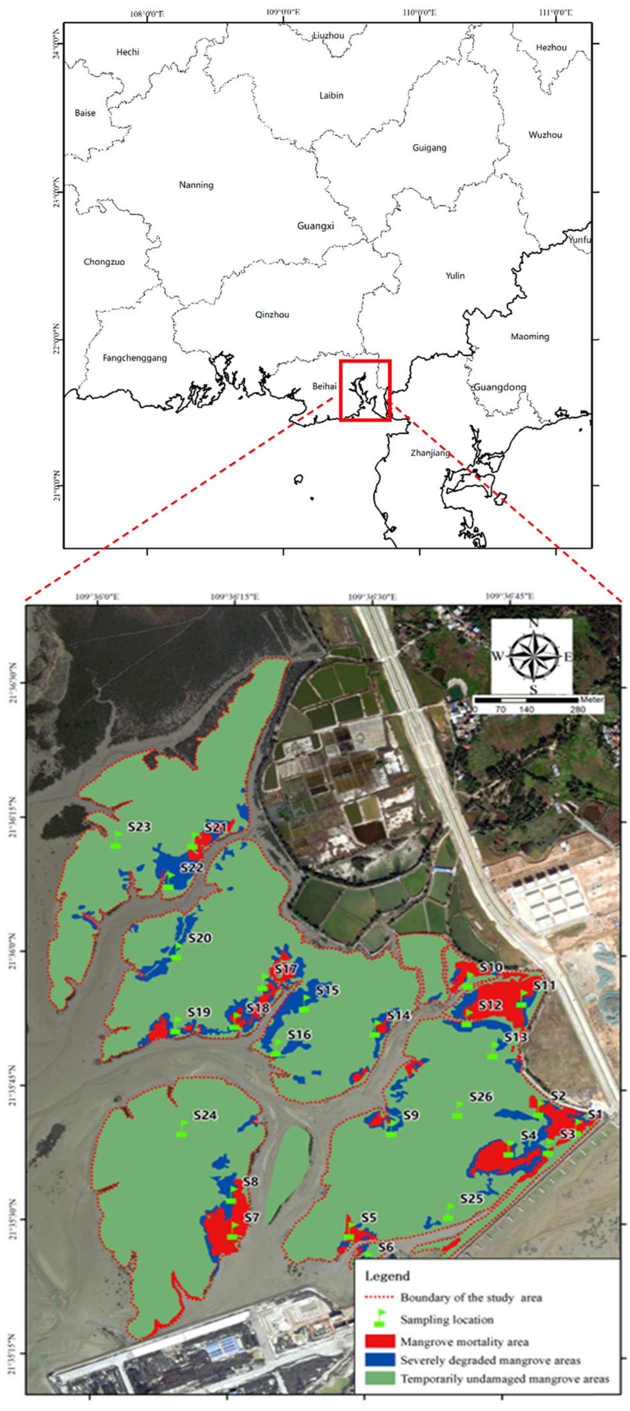

Figure 1: Description of the area of study and sampling sites of the mangrove forest near Langen village of Tieshan Harbor.

2.3 Analytical methods

The sample weighing 0.1000 g was added with mixed acids (HNO_3–$HClO_4$–HF), and placed on a microwave disintegrator to disintegrate, and then an inductively coupled plasma mass spectrometer was applied for the determination of Cu, Cr, Zn, Cd, As, Hg, and Pb content in the samples. The precision and accuracy of the method were evaluated through the use of method blanks, sample duplicates, standard reference materials (GBW07401), and spiked sample recovery. The recoveries observed from the standard spiked samples varied between 95 and 105%.

Soil pH was evaluated by preparing a 1:5 (m/v) soil-to-water suspension. The measurements were conducted using a Sartorius pH meter (model PB-10, Germany) for pH assessment (Hanna, HI98192, Italy). Soil moisture content (WC) was evaluated by drying the samples in an oven at 105°C for 24 h. Total organic carbon (TOC) in the soil was quantified utilizing a TOC analyzer.

2.4 Hazard evaluation of sediment toxic metals

2.4.1 I_{geo}

I_{geo} is a quantitative geochemical index proposed by Müller (1979) [18] for assessing the level of pollution of an individual toxic metal in soil and sediment. This study assesses the extent of toxic metal contamination in sediment and soil within a specific region by analyzing the variations in current and pre-industrial levels of toxic metals. Additionally, it quantitatively categorizes the contamination levels of these toxic metals. This method integrates the influences of both anthropogenic activities and natural diagenetic processes on the depositional environment, thereby enhancing the accuracy of the assessment results. The calculation formula is as follows:

$$I_{geo} = \log_2 \frac{W_n}{1.5 \times B_n}$$

where W_n is the measured value of toxic metal (n), B_n represents the geochemical background value for the specific toxic metals with values for Cu at 4.75 mg/kg, Pb at 13.1 mg/kg, Zn at 44 mg/kg, Cd at 0.070 mg/kg, Hg at 0.0230 mg/kg, Cr at 23.5 mg/kg, and As at 4.170 mg/kg. The calibration constant of 1.5 accounts for potential variations in the background levels of toxic metals influenced by diagenetic processes occurring in different locations. The grading criteria for the I_{geo} are shown in Table 1 [19].

2.4.2 PLI

PLI, proposed by Tomlinson et al. in 1980, is a robust evaluation method grounded in soil background values [20].

Table 1: Relationship between I_{geo} and pollution levels

I_{geo}	Pollution situation
$I_{geo} \leq 0$	Unpolluted
$0 < I_{geo} \leq 1$	Mild
$1 < I_{geo} \leq 2$	Moderate
$2 < I_{geo} \leq 3$	Moderately to strongly
$3 < I_{geo} \leq 4$	High
$4 < I_{geo} \leq 5$	Significantly high
$I_{geo} > 5$	Extremely polluted

This methodology addresses the limitations inherent in the Nemero Pollution Index, which tends to disproportionately emphasize the influence of high values on environmental quality. Consequently, the results derived from the PLI provide a thorough overview of the state of toxic metal pollution in soils, calculated as [21,22] follows:

$$C_f^i = \frac{C^i}{C_b^i}$$

$$\mathrm{PLI} = \sqrt[n]{C_f^1 \times C_f^2 \times C_f^3 \ldots . \times C_f^n}$$

where C_f^i index is the contamination coefficient of trace metals I and n represents metal number. The grading criteria for evaluating the PLI are illustrated in Table 2.

2.4.3 Calculation of E_r^i and RI

The Index of Potential Ecological Hazard approach [23] is a sedimentologically based method for assessing toxic metal contamination and the potential hazards it may pose to the ecosystems. The method initially assesses the potential ecological hazards posed by individual toxic metal elements. Subsequently, it determines the overall potential ecological hazards associated with multiple toxic metal elements within a specific region through cumulative summation, which quantifies and corrects for the toxicological effects of toxic metals, their transport and transformation behaviors within the sediment, the susceptibility of a particular assessment location to toxic metal pollution, along with the variations in baseline levels of toxic metals across distinct regions. This method effectively measures and evaluates the possible effects of toxic metals on the environment, allowing for the classification of ecological hazards through quantitative assessment. It has been extensively utilized in research concerning toxic metal contamination across rivers, wetlands, and marine sediments [24,25]

$$E_r^i = T_r^i \times C_f^i = T_r^i \frac{C_s^i}{C_n^i}$$

Table 2: PLI index classification

PLI	Level of contamination
PLI ≤ 1	Unpolluted
1 < PLI ≤ 2	Low
2 < PLI ≤ 3	Moderate
PLI ≥ 3	High

$$\mathrm{RI} = \sum_{i=1}^{n} E_r^i$$

where C_f^i represents the contamination index of element i in sediments, C_s^i is the measured level of element i in sediments, C_n^i is the reference background level of element i in sediments, T_r^i and E_r^i are the toxicity coefficient and the single-factor potential index of ecological hazard of element i in sediments, respectively, and RI is the composite index of ecological hazard of multiple sediment toxic metals.

The coefficients of toxicity [23] for Pb, Cu, Zn, Cd, Hg, As, and Cr are 5, 5, 1, 30, 40, 10, and 2, respectively. The classification criteria for the potential ecological hazards for E_r^i and RI are illustrated in Table 3.

2.4.4 Sediment environmental quality baseline

To gain deeper insights into the potential biotoxicity of sediments within aquatic ecosystems, this study employed the sediment quality benchmarks for the environment (SQGs). These benchmarks were initially introduced by MacDonald et al. in 2000 [26]. This benchmark is grounded in the concept of critical values, which delineate the probability of adverse biotoxic effects on benthic organisms residing in sediments as a result of toxic metal levels. The more widely used SQGs include critical effect levels at low contamination, called threshold effect levels (TEL), and high probability effect levels at high contamination, called probable effect levels (PEL). In general, adverse biological effects are unlikely to occur when toxic metal levels

Table 3: Classification criteria of ecological hazard index (E_r^i) and toxicity response index (RI)

Potential (E_r^i)	Toxicity (RI)	Level of ecological hazard level
$E_r^i < 40$	RI < 150	Low hazard
$40 \leq E_r^i < 80$	150 ≤ RI < 300	Moderate hazard
$80 \leq E_r^i < 160$	300 ≤ RI < 600	Considerable hazard
$160 \leq E_r^i < 320$	—	High-hazard
$E_r^i \geq 320$	RI ≥ 600	Very high hazard

Table 4: Statistical summary of toxic metal levels (mg/kg)

	Hg	Zn	Cu	Cr	As	Pb	Cd
Minimum (mg/kg)	0.045	7.9	2.2	45.6	3.49	17.1	0.04
Maximum (mg/kg)	0.462	50.3	14.4	195	11.10	85.9	0.19
Average (mg/kg)	0.086	37.97	8.69	121.57	8.59	38.35	0.10
Standard deviation (mg/kg)	0.08	10.53	3.32	40.09	1.85	12.14	0.04
Variation coefficient (%)	93.85	27.74	38.24	32.98	21.51	31.65	37.02
TEL	0.174	124	18.7	52.3	7.2	30.2	0.68
PEL	0.486	271	197	160.4	41.6	112.2	4.21

are below the TEL. However, when levels fall between the TEL and the PEL, such effects may occur occasionally. Once the levels exceed the PEL, the likelihood of adverse biological effects becoming more frequent significantly increases [27].

To quantify and standardize the toxic effects of various toxic metals, the concept of the toxicity units (TUs) index has been introduced. The TU value is calculated by the ratio of the measured level of a toxic metal to its respective PEL [28]. By summing the TUs of the sediment samples, researchers can estimate the possible acute toxicity of toxic metals present in those samples [29].

2.5 Statistical analysis

Pearson correlation coefficient and PCA were carried out using SPSS22.0 software, and spatial interpolation of toxic metal element contents in mangrove sediments at each station in Langen Village, Tieshan Harbor, Guangxi, was carried out by the inverse distance weight method using ArcGIS10.2 software. Origin2021 software was used for the plotting of relevant maps.

3 Results and discussion

3.1 Levels and distribution of toxic metal in sediments

3.1.1 Descriptive statistics of sediment toxic metal content

Table 4 shows the statistical results of toxic metals in the intertidal mangrove sediments near Langen Village in the Tieshan Harbor. The findings indicated that the concentrations of toxic metals in shallow sediment (mg/kg) were 0.045–0.462 for Hg, 7.9–50.3 for Zn, 2.2–14.4 for Cu, 45.6–195 for Cr, 3.49–11.10 for As, 17.1–85.9 for Pb, and 0.04–0.19 for Cd. The mean levels of the seven toxic metals were observed to decrease in the following sequence: Cr (121.57 ± 40.09 mg/kg^{-1}) > Pb (38.35 ± 12.14 mg/kg^{-1}) > Zn (37.97 ± 10.53 mg/kg^{-1}) > Cu (8.69 ± 3.32 mg/kg^{-1}) > As (8.59 ± 1.85 mg/kg^{-1}) > Cd (0.10 ± 0.04 mg/kg^{-1}) > Hg (0.086 ± 0.08 mg/kg^{-1}). The mean levels of Hg, Zn, Cu, and Cd were less than the TEL, indicating that the deleterious biological impacts of toxic metals Cd, Hg, Cu, and Zn in the intertidal mangrove sediments near Langen Village in the Tieshan Harbor were mild. However, the average levels of Cr, As, and Pb fell between the TEL and the PEL, indicating that there is a certain probability that a toxic effect may develop and have a toxic effect on organisms. The coefficient of variation serves as an effective indicator for assessing the extent of spatial dispersion of toxic metals in sediment [30], and the statistical results displayed that the coefficient of variation of Hg content was 93.85%, which was highly variable, and the coefficients of variation for the levels of the remaining six toxic metals varied from 10 to 90%, which showed moderate variability. Table 5 compares the mean of the heavy metal concentrations in sediments from this study with the domestic and global mangrove ecosystems. Cu and Zn concentrations in the sediments were lower than those reported in other mangrove ecosystems worldwide, whereas Cr levels exceeded the corresponding values from global mangrove sediment studies. Pb concentrations significantly surpassed those in international mangrove ecosystems but remained lower than those documented in Zhanjiang Bay mangroves, China.

3.1.2 Spatial distribution of sediment toxic metals

Spatial temporal analysis revealed distinct heavy metal distribution patterns in Langen Village's intertidal mangrove sediments (Tieshan East Harbor). Maximum concentrations of Cr, Pb, Cu, and Zn were concentrated in

Table 5: Comparative analysis of heavy metal concentrations (mg/kg) in mangrove sediments from the Eastern Port Area of Tieshangang Harbor, Guangxi, with domestic and international regions

Study area	As	Cd	Pb	Zn	Cu	Cr	Hg	Reference
Tieshangang Harbor	8.59	0.1	38.35	37.97	8.69	121.57	0.086	The present study
Zhanjiang Bay	—	—	105	352	400	74.3	—	[31]
Sundarbans	—	—	25.44	62.85	47.67	23.4	—	[32]
Bangladesh	—	—	7.38	62.32	35.74	36.6	—	[33]
Cocin estuary	—	5.85	24.15	866.2	22.97	6.64	—	[34]

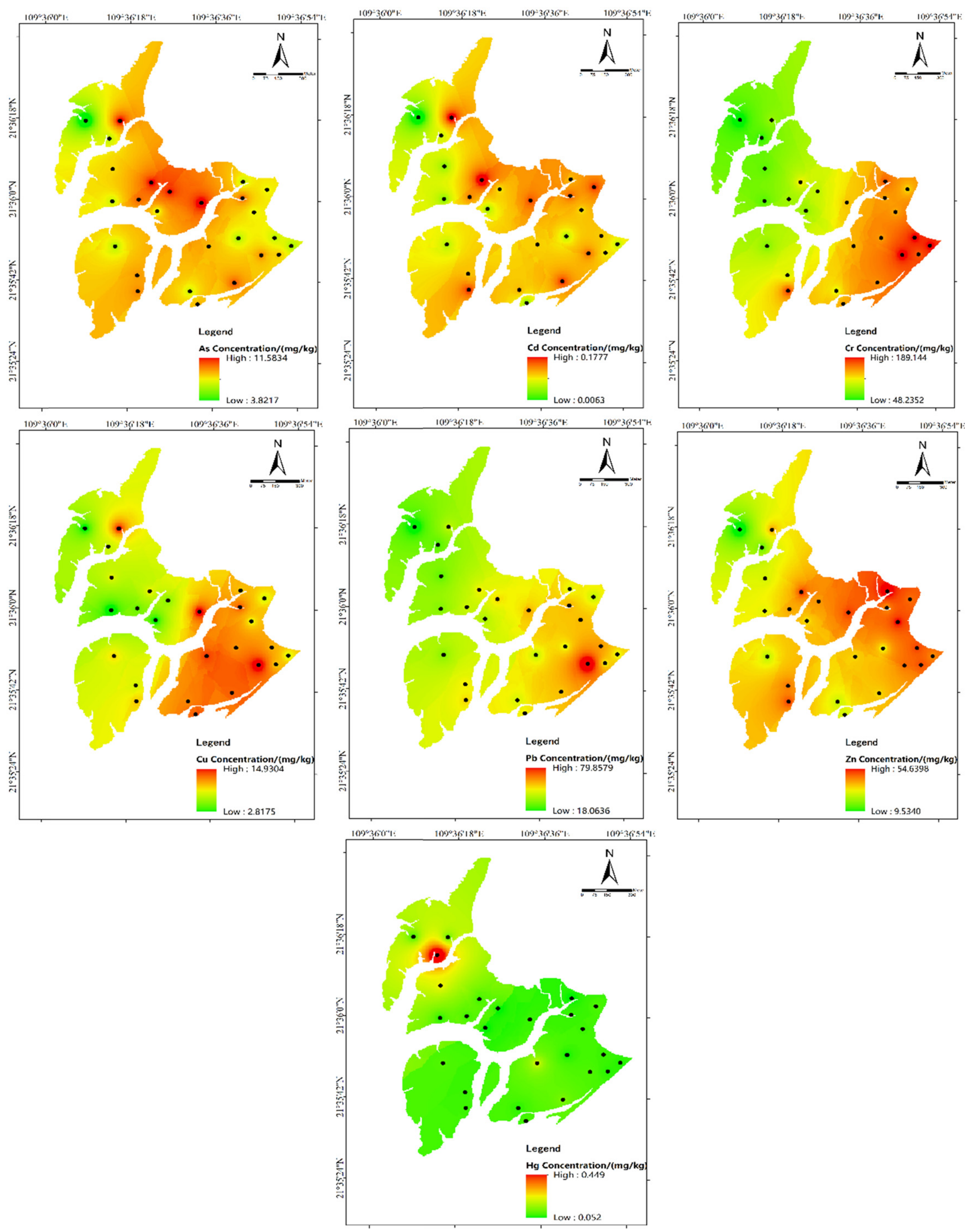

Figure 2: Distribution across space of toxic metals in the surface sediments in mangrove of intertidal zones near Langen Village.

southeastern zones (Figure 2) proximal to ongoing reclamation activities and tidal channels. Hg maxima were recorded in northern sectors, while enhanced As and Cd concentrations predominated in northeastern and southeastern regions. These hotspots coincide with hydrologic exchange conduits linking terrestrial discharge points to mangrove ecosystems, particularly pathways for terrigenous material inputs including excavated soils and dredged sediments. This spatial correlation aligns with established sediment contamination patterns showing significant heavy metal enrichment near riverine pollution sources [25,35]. Crucially, the most contaminated zones across all seven metals exhibited strong spatial correspondence with dead and severely degraded mangrove stands.

In recent years, offshore construction activities including channel dredging and wharf berth construction have been conducted in the eastern port area of Tieshan Harbor. These anthropogenic disturbances have led to the dispersion of fine-grained particles such as kaolinite into the seabed, which are subsequently transported by tidal currents to the mangrove areas near Langen Village and its surrounding regions during flood tides. Li et al. [36] demonstrated that kaolinite suspensions exhibit higher deposition rates in proximity to reclamation areas or tidal channels. Notably, Cu, Pb, and Cr concentrations in sediment substrates of mangroves impacted by kaolinite suspensions were approximately twice those observed in unaffected mangrove systems. Additionally, Pb content in substrates of tidal channels influenced by kaolinite suspensions was found to be double that of control tidal channel areas lacking such suspensions. Commonly, kaolinite is capable of adsorbing toxic metal ions through two primary mechanisms: ion exchange and surface coordination [37,38]. Therefore, kaolinite dispersal caused by offshore construction activities in this region can be deposited into mangrove forest through tidal exchange under hydrodynamic effects, further exacerbating the hazard of toxic metal accumulation in the mangrove substrate. Moreover, the migration, transformation, and distribution across space of toxic metals are also subject to the comprehensive constraints of sedimentary biogeochemical characteristics and hydrodynamic conditions [39–41]. Physical and chemical characteristics of sediments including grain size composition, pH, organic fraction, redox potential, dissolved oxygen level, sulfides, etc., significantly influence the material exchange of toxic metals among sediments, pore water, and the overlying water [42–44].

3.2 Evaluation of the levels of sediment toxic metal contamination

3.2.1 Evaluation of trace metal contamination

As illustrated in Figure 3, the I_{geo} values for seven toxic metals in 26 sampling sites in intertidal mangrove sediments near Langen Village are calculated. The mean I_{geo}

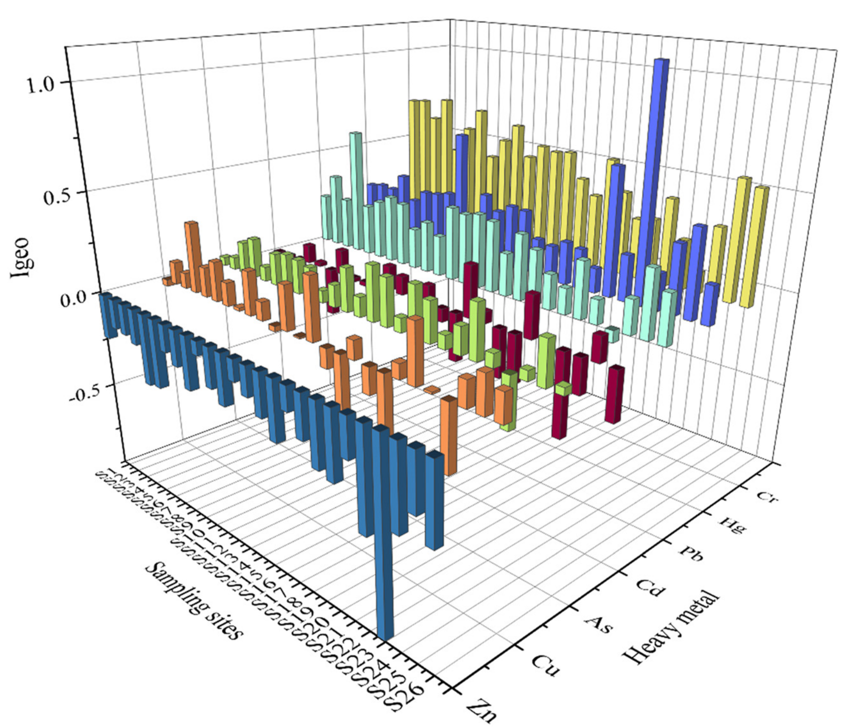

Figure 3: I_{geo} values of toxic metal elements in the surface sediments in mangrove of intertidal zones near Langen Village.

values in mangrove sediments were Cr (0.512) > Hg (0.326) > Pb (0.273) > As (0.127) > Cu (0.048) > Cd (−0.046) > Zn (−0.264). The pollution levels of the seven toxic metals exhibited significant variation across the different sampling sites. Zn was in a non-polluted state in all sampling points in the region, while Cr was in a slightly polluted level in all sampling points in the study area. Only one site (S22) exhibited moderate pollution levels for Hg (I_{geo} = 1.13), while all other sampling points were classified as slightly polluted levels. Pb and As were in a slightly polluted level in most of the sampling points, except for one site (S23) which showed a non-polluted state. The slightly polluted points of Cu and Cd accounted for 69 and 38%, respectively. Furthermore, based on the distribution across space of the sampling points, we found that the polluted stations were mostly distributed in the dead mangrove and severely degraded mangrove area. Overall, pollution levels of Pb, Hg, and Cr were most pronounced in the mangrove sediments near Langen village in Tieshan Harbor.

The PLI of the seven trace metals across all sampling sites is illustrated in Figure 4. The PLI values for the toxic metals varied between 0.89 and 3.09, with an average of 2.13. This finding suggests that the level of contamination of sediment toxic metals in this region is moderate.

3.2.2 E_r^i and RI

Figure 5 shows the potential index of ecological hazard of each toxic metal. The single potential ecological hazard of E_r^i values ranged between 0.18 and 1.28 for Zn, between 3.58 and 16.63 for Cu, between 3.88 and 16.60 for Cr, between 8.37 and 28.06 for As, between 6.53 and 17.79 for Pb, between 21.43 and 81.43 for Cd, and between 78.26 and 803.48 for Hg. Taking into account the total toxic metals examined, the E_r^i for these toxic metals was ranked in the following order: Hg (150.17) > Cd (43.35) > As (20.61) > Pb (14.64) > Cr (10.35) > Cu (9.15) > Zn (0.86). Moreover, the E_r^i index for As, Pb, Cr, Cu, and Zn across all sampling points was found to be below 40. This indicates a low ecological hazard attributed to their minimal toxicity factors. Cd is at slight and medium potential ecological hazard in the region. Hg has one site (S22) at very high potential ecological hazard and two sites (S9 and S20) at medium possible ecological hazard. It should be noted that according to the results of I_{geo} evaluation, although Cr is the most seriously polluted toxic metal element in the region, its E_r^i value is relatively low due to its low ecotoxicity; whereas Hg and Cd usually have a high toxicity response coefficient and the organisms are more sensitive to them, which results in a

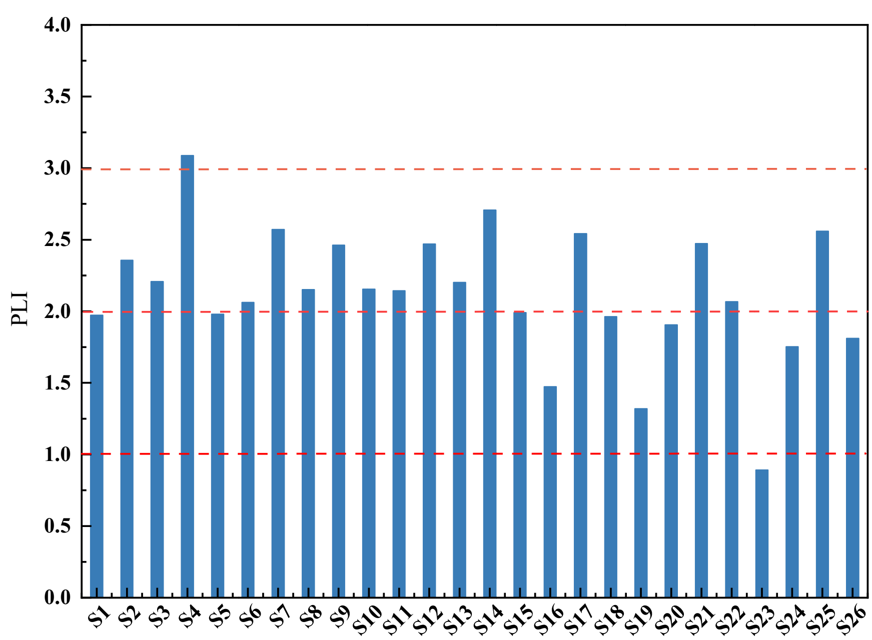

Figure 4: PLI values of toxic metal elements in the surface sediments in mangrove of intertidal zones near Langen Village.

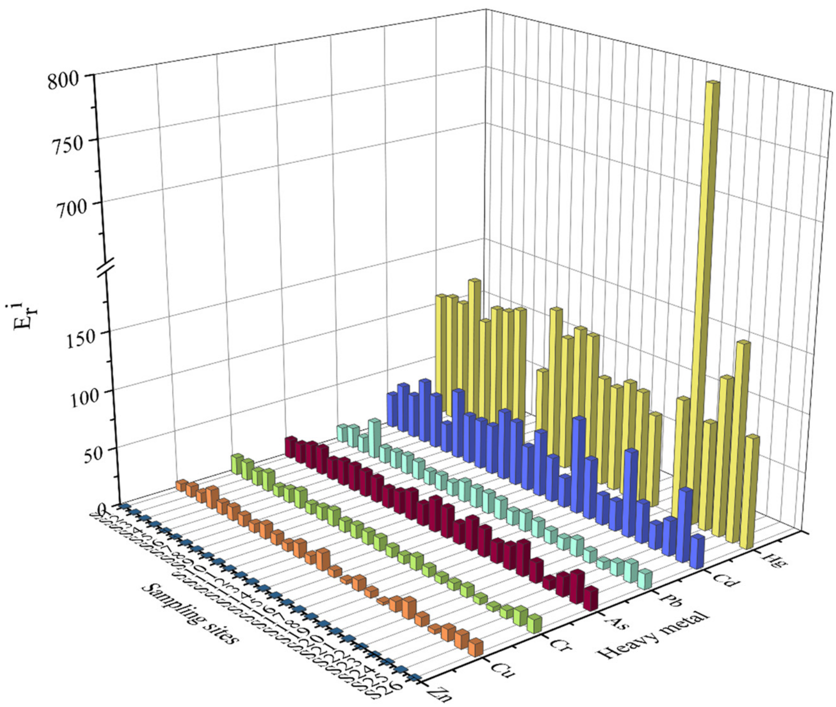

Figure 5: E_r^i of toxic metals in the surface sediments in mangrove of intertidal zones near Langen Village.

greater potential hazard to the ecosystems, especially Cd, which is at a relatively low level of contamination in this study, but its potential ecological hazard is second only to Hg and is considerably greater than that posed by other toxic metals.

Figure 6 shows the ratio of RI contribution of the possible hazard associated with each single toxic metal across all sampling sites. The RI ranges of all sampling sites were 143.6–878.7, with a mean value of 249.3, reflecting medium potential ecological hazard within the study area.

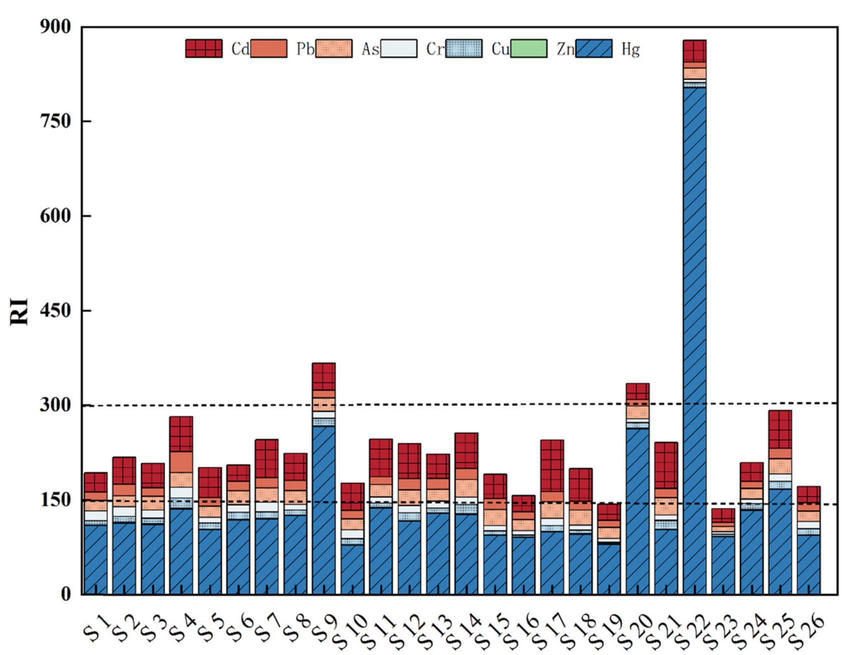

Figure 6: RI of trace metals in the surface sediment in mangrove of intertidal zones near Langen Village.

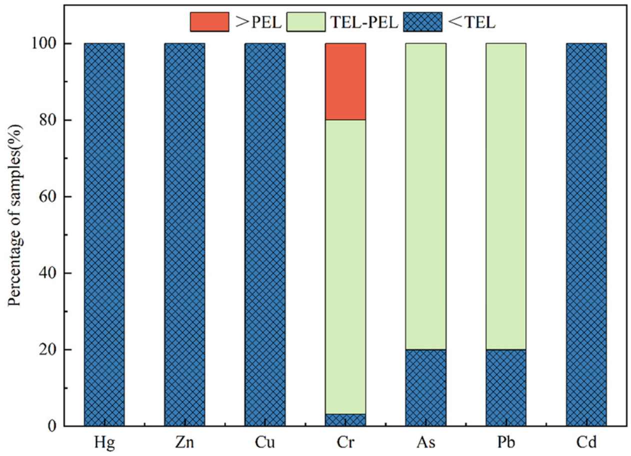

Figure 7: Percentage of sample size based on TEL and PEL.

Relatively elevated RI levels (300 ≤ RI < 600) were observed at two specific sites, namely S9 and S20, manifesting the presence of a strong potential ecological hazard. Overall, Hg predominated as the principal driver of the RI, with Cd and As exhibiting secondary but non-negligible contributions. These findings collectively indicate that Hg, Cd, and As constitute critical ecological hazard factors in the study area, necessitating their prioritized integration into regional environmental monitoring frameworks. Notably, Hg demonstrates exceptionally elevated ecological hazard potential within marine ecosystems, highlighting the urgency for targeted regulatory measures to mitigate its environmental dispersal and bioaccumulation risks.

3.2.3 Toxic hazard index

Figure 7 shows the statistics of the proportion of samples with different toxic metal contents in the three interval segments based on TEL and PEL. The maximum levels of toxic metal elements did not exceed the PEL level except for Cr. All the samples of Hg, Zn, Cu, and Cd were below the TEL, 80% of the samples of both As and Pb were in the range of TEL–PEL, and 19% of the samples of Cr exceeded the PEL levels, all of which were located in dead mangrove areas.

As can be seen in Figure 8, the ΣTUs of sediments at each sampling point were less than 4, indicating that the biotoxic effects caused by toxic metal elements in sediments in the region were low. In addition, as a whole, the mean TUs at each sampling point was Cr > Pb > As > Hg > Zn > Cu > Cd, indicating that Cr, Pb, and As contributed more to the ΣTUs, which ranged from 20.87 to 58.43%, from 15.20 to 28.90%, and from 8.18 to 17.17%, respectively.

3.3 Sources and impact mechanisms of sediment toxic metals

Through PCA, HCA, and factor analysis (FA) the plausible sources of sediment toxic metals as well as the influence mechanisms could be traced. As shown in Figures 9, 10 and Table 6, three principal components were extracted, of which the KMO value was 0.82, the Bartlett value was

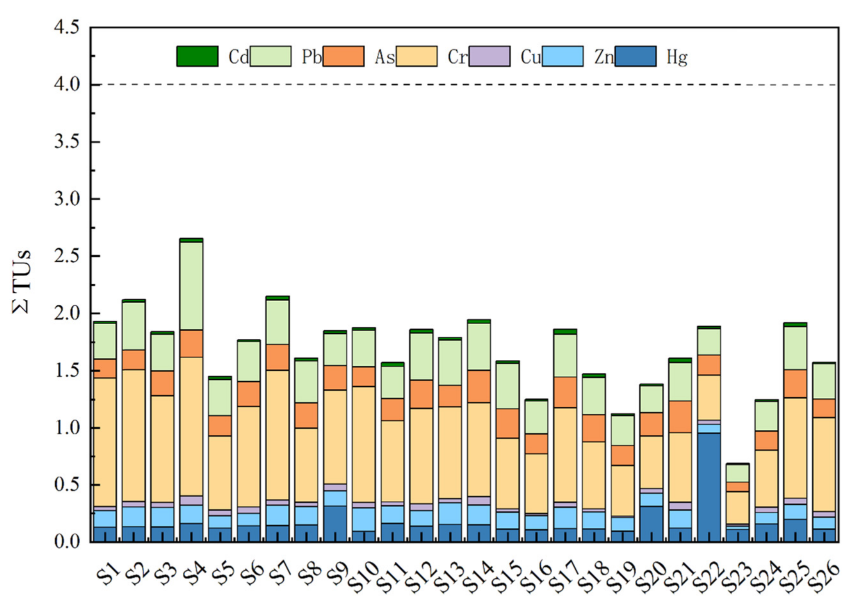

Figure 8: ΣTUs of trace metals in the surface sediment in mangrove of intertidal zones near Langen Village.

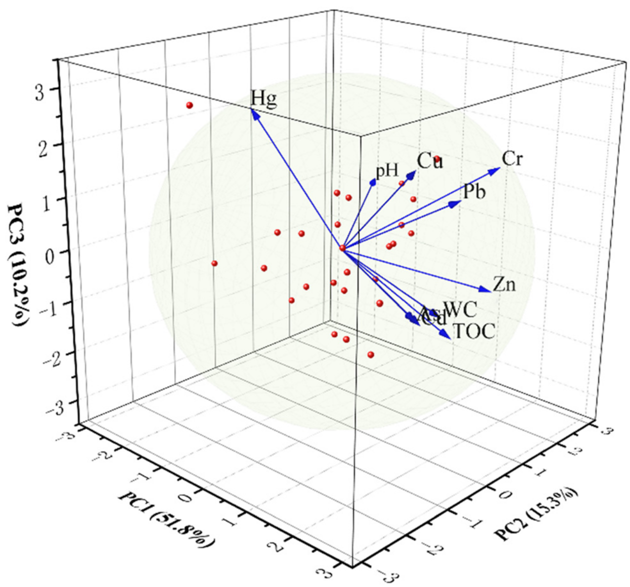

Figure 9: Results of PCA for identifying sources in the surface sediment in mangrove of intertidal zones near Langen Village.

174.06, and the significance level was 0.003, which indicated that the results of the data were credible. The principal factors (PCs) were responsible for 77.30% of all variable variance. The first factor (PC1) was mainly related to As, Cd, TOC, pH, and WC and was responsible for 51.804% of the variance. The second (PC2) represents 15.31% of the variance and showed a highly positive loading of Zn, Cu, Cr, and Pb. The third (PC3) was responsible for 10.19% of the total variance and it completely recorded a positive loading of Hg. The results of HCA showed that the surface sediments in the mangrove forests of this region can be divided into three main clusters, which is consistent with the results of the PCA.

In general, the distribution across space of toxic metals in sediments is regulated by the combination of external anthropogenic and terrestrial sources, as well as the hydrological conditions of the region [25]. Elevated concentrations of As and Cd predominantly clustered along terrestrial drainage outlets. Field investigations identified 29 drainage outlets in mangrove peripheries, some of which have inadequate protective structures and compromised erosion resistance. These substandard configurations facilitate terrestrial soil transport into mangrove ecosystems during high-intensity precipitation events. In addition, aquaculture ponds are distributed east of the mangrove forests, where the discharge of feed residues, veterinary pharmaceuticals, and domestic sewage from these operations may contribute to toxic metal contamination [45], suggesting that PC1 profiles likely reflect land-source discharges from integrated aquaculture-sewage systems, such as aquaculture wastewater, domestic sewage, and industry drainage. The high value area of Zn, Cu, Cr, and Pb were predominantly distributed near the southeastern land reclamation areas and wharf berth construction zones. We infer that PC2 primarily reflects pollution from land reclamation activities, including foundation trench excavation, rock dumping for foundation trenches, and overflow from land reclamation [46]. Elevated Hg concentrations were concentrated in areas adjacent to industrial parks and the coastal front of Tieshan Harbor's eastern port, where coal-fired power plants and glass/quartz sand manufacturing facilities are clustered. Additionally, given the ongoing navigation channel dredging projects in Tieshan Bay, PC3 likely represents composite pollution sources such as ship emissions, coal combustion effluents [47], leakage from sand washing facilities, and dredged material stockpile releases (Table 6).

As shown in Figure 11, the correlations between seven toxic metals and the physicochemical properties of

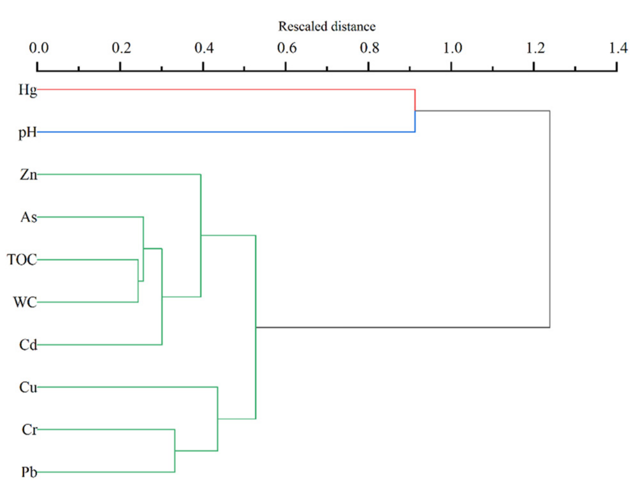

Figure 10: HCA of the toxic metal content in the surface sediments.

Table 6: Results of FA

Variable	PC1	PC2	PC3
Hg	0.166	0.188	**−0.836**
Zn	0.280	**0.630**	0.569
Cu	0.556	**0.626**	−0.299
Cr	0.116	**0.935**	0.225
As	**0.639**	0.595	0.169
Pb	0.411	**0.731**	0.122
Cd	**0.756**	0.314	0.212
TOC	**0.681**	0.398	0.410
pH	**−0.836**	0.188	0.166
WC	**0.726**	0.415	0.265
Initial eigenvalues	5.180	1.531	1.019
Percentage of variance	51.804	15.306	10.193
Cumulative percentage	51.804	67.110	77.303

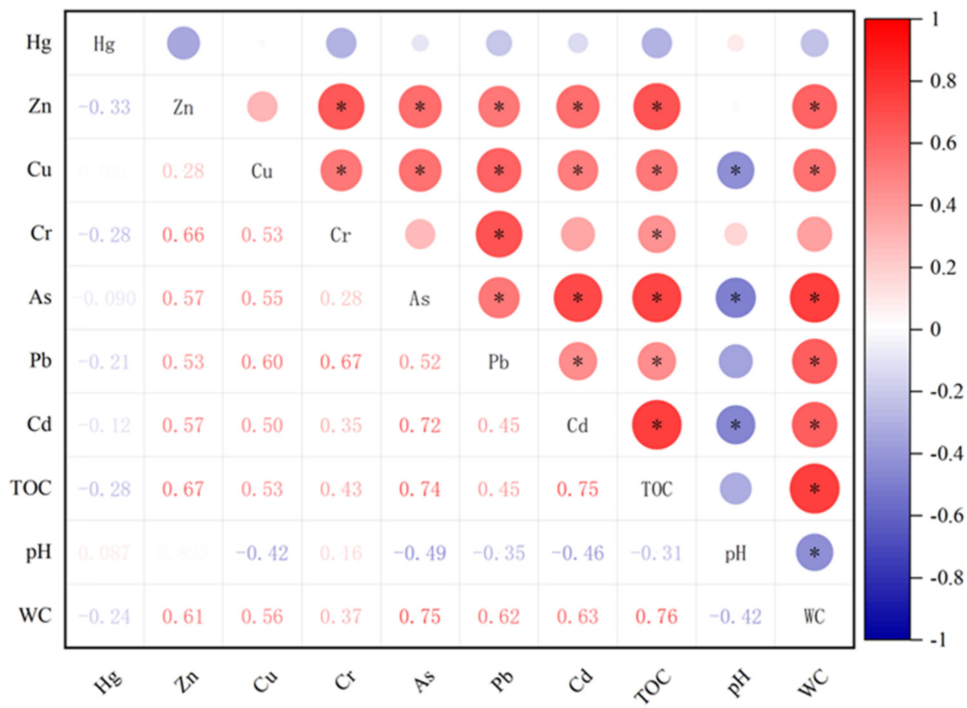

Figure 11: Correlations between soil physical and chemical properties and toxic metal content in the surface sediments in mangrove of intertidal zones near Langen Village. The correlation matrix between different indicators, $n = 26$. * represents a significant difference ($p < 0.05$) and ** represents an extremely significant difference ($p < 0.01$).

sediments were analyzed by Pearson coefficients. The levels of Cu, As, Pb, Cd, Zn, and Cr showed a significant positive correlation ($p < 0.05$) with both TOC and WC except for Hg. This finding is consistent with the fact that organic matter can increase the retention capacity of toxic metals through adsorption, cation exchange, and chelation reactions and produce ligands that cannot be absorbed by the root system, which enhances the retention capacity of toxic metals within sediments through the presence of organic matter [48]. pH was negatively correlated with Cu, As, Pb, Cd, and Zn except for Hg and Cr. Zhou et al. [49] observed that elevated pH levels promote the formation of soluble complexes of toxic metals with dissolved organic carbon or facilitate their release through the dissolution of sulfides. This process results in a reduction of toxic metal concentrations in sediments. Additionally, all metals showed only a weak correlation with Hg, suggesting that sources of Hg are different from other toxic metals.

4 Conclusions

The levels of shallow sediment toxic metals in mangrove of intertidal zones near Langen Village in Tieshan Harbor were ranked as Cr > Pb > Zn > Cu > As > Cd > Hg. The mean levels of Hg, Zn, Cu, and Cd less than the TEL, and those of Cr, As, and Pb between the TEL and the PEL. Most of the high value areas of the seven toxic metals were distributed in the dead and severely damaged mangrove areas. The coefficient of variation of Hg content was 93.85%, which was highly variable, and the remaining six toxic metals showed moderate variability. The mean value of I_{geo} index was Cr > Hg > Pb > As > Cu > Cd > Zn. PLI index indicated that the toxic metal contamination of mangrove sediments in the region was at moderate level. EI index indicated that Hg was at strong potential ecological hazard, and the results of the RI analysis showed that the overall mangrove sediments in the region showed medium potential ecological hazard. Meanwhile, the ΣTUs of the sediments at each sampling point were less than 4, indicating that the biotoxic effects caused by toxic metal elements in the sediments in this region were low. The main sources of As and Cd in the mangrove sediments near Langen Village were land-based pollutants discharged into the sea. Zn, Cu, Cr, and Pb were related to the reclamation activities. Meanwhile, the main source of Hg was the combined pollution factors of ship navigation, discharge from coal-fired power plants, sand washing, and leakage of dredged material from the landfill.

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Ethical approval: The conducted research is not related to either human or animal use.

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