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Depositional record of metal(loid)s since late quaternary in the Laizhou Bay, China

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The contamination of marine ecosystems with metal(loid)s is an increasing environmental concern, largely driven by anthropogenic activities, and poses a significant risk to the health of ecosystems and human well-being. Geochemical background values represent the typical concentrations of trace elements observed in the natural environment. The utilization of disparate background values gives rise to disparate evaluation outcomes. The objective of this study was to investigate the concentration profiles of metal(loid)s (Cu, Pb, Zn, Cr, Cd, As, and Hg) along a sediment core in order to obtain background values and assess the depositional processes and contamination levels in Laizhou Bay. With the exception of arsenic, the distribution patterns of the remaining metal(loid)s were similar and could be divided into four stages, which were primarily influenced by the mean grain size and sediment sources. The results of the analysis of multiple indicators indicated that there was no evidence of heavy metal enrichment or contamination in the core sediments. Furthermore, the data demonstrated that all metal(loid)s present were of natural origin. The historical changes in metal(loid)s in the core sediments were predominantly linked to the sedimentary environment, sediment sources, and mean grain size. The mean values of the metal(loid)s in the DU 4-2 unit, formed during the Early Holocene, may be regarded as reference values for background concentrations.

KEYWORDS

metal(loid)s, core sediment, sediment contamination, late quaternary, Laizhou Bay (China)

1 Introduction

Metal(loid)s are among the major chemical substances that cause environmental pollution (Gil and Olmedo, 2023; Thorat et al., 2023). Metal(loid)s have wide-ranging sources, long persistence, difficult degradation, difficult detection and recovery after pollution, and easy transfer and accumulation along the food chain (Briffa et al., 2020;

Rehman et al., 2021). They can directly or indirectly affect the DNA of organisms, causing the abnormal development of marine organisms and even the extinction of sensitive species, resulting in irreversible impacts on ecosystems (Chen et al., 2016; Li et al., 2022). Heavy metal indicators in seawater and sediments are important components of marine environmental assessment (Onakpa et al., 2018; Sánchez et al., 2020; Strode et al., 2017).

Laizhou Bay is located northwest of the Shandong Peninsula and in the southern part of the Bohai Sea, covering an area of approximately 6000 km^2 (Yuan et al., 2023). It is a typical semi-enclosed coastal bay and an important fishing area in China. Several rivers discharge into the sea, such as the Yellow, Xiaoqing, Bailang, Wei, and Jiaolai rivers, and carry large amounts of sediment pollutants every year (Duan et al., 2021). With the rapid economic development in the area, the combination of multiple human activities, such as land-based pollution, land reclamation projects, port shipping, and fishing, has led to prominent ecological and environmental issues in this sea area. Relevant studies have shown that human activity has increased the heavy metal content of sediments in the Bohai Sea (Wu et al., 2022). In addition, changes in land-based pollution and water dynamics in the bays and estuaries of the Bohai Sea have significantly influenced the deposition and distribution of metal(loid)s in sediments, potentially causing corresponding changes to the ecological environment.

Extensive research has been conducted on the characteristics of heavy metal pollution and ecological risks in the sediments of Laizhou Bay, based on large amounts of surface sediment (Li et al., 2013; Duan et al., 2021; Wu et al., 2022). However, there are some differences in the results of different studies, especially in the evaluation of heavy metal pollution and ecological risks, owing to the lack of unified background values. For example, when assessing heavy metal pollution in Laizhou Bay, as the background values, Xu et al. (2015) used the concentration of metal(loid)s in Bohai sediment, Duan et al. (2021) used the content of soil elements in Shandong Province, and Xu et al. (2021) selected the concentration of metal (loid)s in Bohai sediment and the concentration of metal(loid)s in adjacent land soil in Shandong Province, and then compared and analyzed the differences in the calculation results. Therefore, using multiple evaluation methods and combining them with historical changes in heavy metal content will provide a more objective and comprehensive understanding of the metal pollution status in Laizhou Bay. The historical trends of trace elements in the sediments of Laizhou Bay are poorly understood because of the lack of long drill holes. This study aimed to analyze historical variations in heavy metal content in Laizhou Bay using collected geological borehole data. Multiple evaluation methods were employed to comprehensively assess the status of heavy metal pollution and ecological risk. The goals were to gain a better understanding of heavy metal pollution in Laizhou Bay, identify characteristic pollutants, provide reference values for selecting background values of metal(loid)s in the study area, and provide a scientific basis for preventing and controlling heavy metal pollution in related marine areas and for the comprehensive management of the Bohai Sea.

2 Materials and methods

2.1 Sampling and analytical methods

The sediment core LZ01 (119.8413°E, 37.8316°N; Figure 1) was collected in 2013 using a rigging drill. The sediment core, measuring 70.1 meters in length, was obtained at a water depth of 17.82 meters. The average core recovery rate was 86.8%. The core was split lengthwise, described visually, and subsequently sub-sampled in the laboratory. A total of 261 subsamples were taken from the core LZ01 at 25–30 cm intervals for grain size and elemental analyses. The samples were treated and tested in accordance with the methodology described by Xu et al. (2015). The grain size properties were calculated in accordance with the formula proposed by Folk and Ward (1957). The quality of the elemental analysis was evaluated using parallel samples and the national sediment standard GBW07309 (GSD-9), which was analyzed for every 10 unknown samples. The relative error of the parallel samples was determined to be less than 5%.

The selection of gastropods and unbroken shells, including the peat layers, for accelerator mass spectrometry (AMS) 14C dating (Stuiver et al., 2020) is presented in Table 1. Nine samples from core LZ01 were collected for optically stimulated luminescence (OSL) dating of quartz, employing a Daybreak 2200 thermoluminescence/OSL reader (Table 2). The concentrations of K, U, and Th were determined through inductively coupled plasma mass spectrometry and subsequently converted into dose rates, with the requisite data sourced from Aitken (1998) and Marsh et al. (2002).

2.2 Assessment methods of heavy metal pollution

2.2.1 Enrichment factor

The enrichment factor (EF) is a quantitative indicator that is employed to evaluate the extent of heavy metal contamination in sediments and to ascertain its sources (Marmolejo-Rodríguez et al., 2017). By utilizing aluminum as a reference element, the elemental composition of the sample was normalized in order to eliminate the impact of variations in particle size (Zhou et al., 2022).

EF values were calculated using Equation 1:

$$EF = (Me/Al)_{sample}/(Me/Al)_{baseline} \quad (1)$$

where Me_{sample} and Al_{sample} are the trace element and Al concentrations in each sample, respectively, and $Me_{baseline}$ and $Al_{baseline}$ are the reference element concentrations. According to Xu et al. (2015), the sediment in the study area was primarily from the material discharged by rivers along its western and southern coasts. Therefore, the elemental background concentrations in the soil of Shandong Province were adopted to calculate the EF values in this study (CNEMC, 1990). EF < 1.5 is indicative of metal(loid)s related to crustal sources, whereas EF > 1.5 implies anthropogenic sources (Zhang and Liu, 2002).

FIGURE 1
Location of the core LZ01 in the Laizhou Bay.

2.2.2 Geoaccumulation index

The geoaccumulation index (I_{geo}) is used to eliminate the influence of natural geological contributions, and is calculated using Equation 2:

$$I_{geo} = \log_2(C_n/(1.5 \times B_n)) \quad (2)$$

In accordance with the findings of Muller (1981), seven categories of geoaccumulation indices were identified, spanning from class 0 ($Igeo \le 0$, unpolluted) to class 7 ($Igeo > 5$, extremely polluted).

2.2.3 Potential ecological risk index

The potential ecological risk index (E_R) evaluates the degree of heavy metal contamination in sediments based on the potential toxicity of metal(loid)s and the environmental response. E_R was calculated as follows:

$$C_r^i = C_f^i/C_n^i, E_r^i = T_r^i \times C_r^i, E_R = \sum E_r^i \quad (3)$$

The potential ecological risk coefficient for each heavy metal was calculated as follows: 1 for Zn, 2 for Cr, 5 for Cu and Pb, 10 for As, 30 for Cd, and 40 for Hg (Hakanson, 1980). The comprehensive

TABLE 1 AMS^{14}C ages in core LZ01.

Depth (m)	Materials	δ^{13}C (permil)	Conventional age (^{14}C yr BP)	Calendar ages(Cal yr BP)	
				Intercept	Range (2σ)
6.83	Gastropod	-2.3	8310 ± 40	9102	9012-9191
8.40	Gastropod	-4.8	8350 ± 40	9159	9065-9253
10.46	Peat layer	-22.9	8720 ± 40	9649	9563-9734
10.64	Shell	+4.1	8610 ± 40	9459	9405-9512
20.87	Gastropod	-3.4	> 43500		
31.77	Gastropod	+1.8	> 43500		
38.31	Gastropod	+2.2	> 43500		
45.44	Gastropod	+4.2	> 43500		

TABLE 2 OSL ages in core LZ01.

Depth (m)	Materials	Water content (%)	U (ppm)	Th (ppm)	K (%)	DE (Gy)	Age (ka)
13.50	Quartz	15.89	3.68	9.53	1.54	82.1	16.6 ± 2
16.27	Quartz	16.97	2.75	6.70	1.59	102.2	24.9 ± 2
18.63	Quartz	14.39	2.39	7.97	1.73	106.5	25.1 ± 3
23.63	Quartz	23.70	3.08	11.7	1.66	131.5	26.2 ± 3
35.59	Quartz	20.58	2.10	6.27	1.78	155.5	40.3 ± 4
44.77	Quartz	16.59	3.07	10.4	1.86	219.8	43.2 ± 4
48.18	Quartz	24.26	2.54	6.85	1.56	205.1	52.5 ± 5
62.31	Quartz	21.55	2.89	12.2	1.71	256.9	55.7 ± 6
66.59	Quartz	18.99	1.84	7.39	1.54	277.2	75.8 ± 7

potential ecological risk index for multiple metal(loid)s is represented by E_R. Each heavy metal was classified into one of five categories based on its potential ecological risk (E_r^i): low (less than 40), moderate (40-79), considerable (80-159), high (160-319), and very high (equal to or greater than 320) ecological risk. The E_R was classified into four levels: low ecological risk ($E_R < 105$), moderate ecological risk ($105 \le E_R < 210$), significant ecological risk ($210 \le E_R < 420$), and very high ecological risk ($E_R \ge 420$) (Xu et al., 2021).

3 Results

3.1 Sedimentary structure of the core

The general stratigraphic framework of core LZ01 was identified through a process of correlation involving the application of AMS^{14}C and OSL ages, sedimentary structures, sedimentary facies, grain size, and comparison with other well-studied cores from adjacent areas. The core was subdivided into four units, designated DU1–DU4, in descending order (Figures 2, 3).

DU 1 (70.10–51.87 m) was primarily composed of dark gray, dark yellow-gray, earthy yellow silt, and clayey silt, interspersed with clayey bands and silt lenses. Calcium nodules and brownish-yellow rust spots are visible, indicating moderate biological disturbance. Locally, there are gray-yellow to yellow-gray fine to medium sands, with average sorting. The sediment exhibits cross-bedding and contains minor clayey bands, along with occasional black spots and rust stains. The sediment composition is predominantly silt, with an average content of 54.86%, followed by sand at an average of 32.92%, with a maximum content reaching 94.23%. Clay content is the least, ranging from 0% to 37.85%, with an average of 12.21%. The average grain size varies significantly, ranging from 3.05 to 7.55 Φ, indicating considerable changes in the sedimentary environment, with an average of 5.17 Φ. The OSL dating for this unit yields relatively young and unreliable ages. Comparisons with surrounding boreholes suggest that the sedimentary environment corresponds to a coastal-marine transitional setting prior to the Late Pleistocene, which maybe formed during marine isotope stage (MIS) 6-7.

DU 2 (51.87–19.03 m) consists mainly of dark gray, dark yellow-gray, dark gray, and earthy yellow clayey silt and silt, with locally dense interlayers and irregular silt to fine sand lenses. A few brown rust spots are visible, along with intact small gastropods. The central area features yellow-gray fine to medium sand, with average sorting and cross-bedding, interspersed with irregular clayey bands. Shell layers are observed at depths of approximately 31.6 m, 33.6 m, 40.8 m, and around 51.8 m, containing abundant shell fragments and intact small gastropods. The sediments are primarily silt and sand, with average contents of 46.59% and 44.16%, respectively, while clay content is minimal, ranging from 0% to 35.63%, with an average of 9.25%. The average grain size also exhibits significant variability, ranging from 3.05 to 7.51 Φ, indicating substantial changes in the sedimentary environment, with an average of 4.69 Φ. The AMS ^{14}C dating of four intact gastropods from the top to the bottom of this unit yields ages greater than 43,500 years. The OSL dating data is similarly young and unreliable. Comparisons with surrounding boreholes indicate that the OSL ages for the corresponding segment of borehole WFZK07 range from 34.7 ± ka to greater than 110 ka. The sedimentary environment of this unit is interpreted as a coastal to shallow marine setting, corresponding to the sedimentary layers formed during the Cangzhou and Xianxian transgressions, which formed during MIS 3-5.

The DU 3 unit (19.03–10.66 m) primarily consisted of dark gray, dark yellow-gray, yellow-gray, and ochre-colored silt to fine to medium sand, with generally poor sorting. It exhibits no distinct layering, interspersed with clay-rich bands, and occasionally contains black carbon spots and a small amount of brown rust stains. The sediment composition is predominantly silt and sand, with silt content ranging from 15.60% to 62.68%, averaging 48.21%. Sand content varies between 18.48% and 81.70%, with an average of 39.95%. Clay content is minimal, averaging 11.84%. The average grain size ranges from 3.47 to 5.91 Φ, with a mean of 4.95 Φ. Three OSL dating results from the top to the bottom of this unit range from 16.6 ± 2 ka to 25.1 ± 3 ka. The sedimentary environment of this unit is interpreted as a terrestrial river deposition during the Last Glacial Maximum (MIS 2).

The DU 4 unit (10.66–0 m) was divided into two subunits DU 4-2 and DU 4-1. DU 4-2 (10.66-6.80 m) mainly comprised dark gray silt-fine sand, with clayey banding, shells, and gastropods. The bottom layers were characterized by peat and shell fragments, with AMS^{14}C

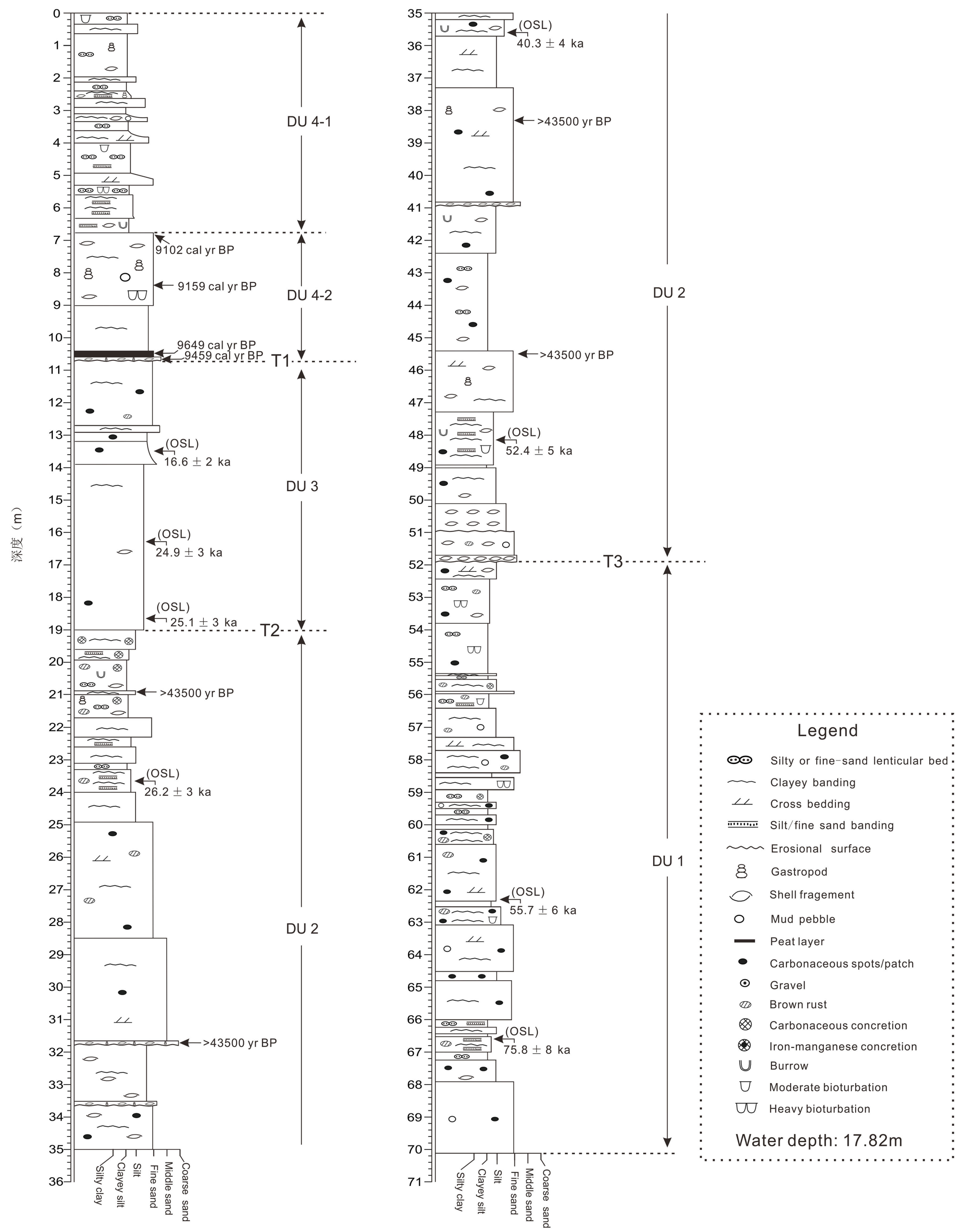

FIGURE 2
Geological column of core LZ01 with AMS^{14}C and OSL.

ages of 9649 cal yr BP and 9459 cal yr BP, respectively. The mean grain size ranged from 4.46 to 5.98 Φ, with an average of 4.94 Φ. This peat layer is a marker of the Holocene bottom of the Bohai Sea. The other two AMS^{14}C ages of the gastropods were 9102 cal yr BP and 9159 cal yr BP. Therefore, this subunit was interpreted as a transgressive deposit formed during the Early Holocene. DU 4-1 (6.80-0 m) was characterized by dark gray clayey silt-silt, with a silt-fine sandy lens. The mean grain size ranged from 4.15 to 7.17 Φ, with an average of 5.90 Φ. No dating data were available for this subunit. From the sedimentary characteristics and stratigraphic correlation with cores BH1302 and WFZK07 in the adjacent area (Figure 3), DU 4-1 was interpreted as shallow marine deposits during the Middle-Late Holocene.

3.2 Concentration of metal(loid)s

The mean Cu, Pb, Zn, Cr, Cd, As, and Hg concentrations in the LZ01 core were 17.36, 19.94, 52.73, 51.41, 0.08, 7.24, and 0.008 mg/kg, respectively (Table 3). The average concentrations of all metal(loid)s were lower than those in the Yellow River estuary (Liu et al., 2023), Dongying coast (Wu et al., 2022), Laizhou Bay (Duan et al.,

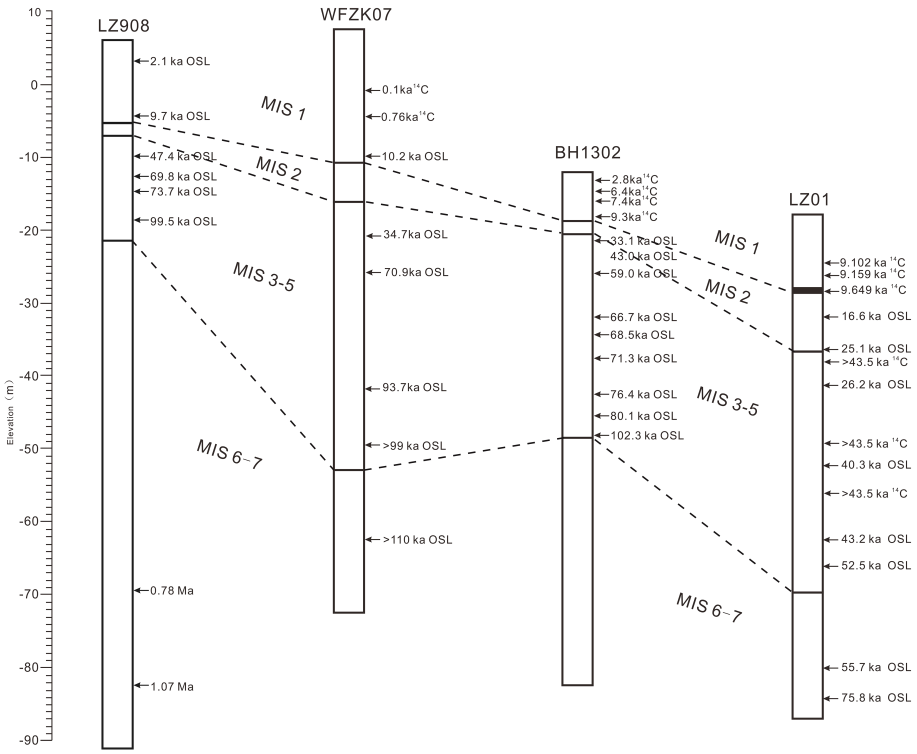

FIGURE 3
Comparison of late Quaternary sediment records from Laizhou Bay cores (BH1302, Yuan et al., 2023; LZ908, Yi et al., 2012; WFZK07, Guo et al., 2017).

TABLE 3 Metal(loid)s concentrations in core sediments (Unit: mg/Kg).

Locations	time	Cu	Pb	Zn	Cr	Cd	As	Hg	References
LZ01	Avg. (n=261)	17.36	19.94	52.73	51.41	0.08	7.24	0.008	This study
	DU4-1	9.1-35.2	15.2-28.3	45-94.8	46.2-76.2	0.053-0.14	5.37-17	0.005-0.018	
	Avg. (n=28)	24.87	22.66	70.67	64.74	0.1	9.83	0.01	
	DU4-2	10.6-24.9	15.4-22.1	40.8-63.1	42.1-68	0.052-0.089	4.32-13	0.005-0.011	
	Avg. (n=15)	16.59	18.01	51.31	50.83	0.07	6.63	0.01	
	DU3	9-24.4	14.8-23.5	37.2-60.1	37.5-61.2	0.046-0.14	2.48-14.4	0.002-0.009	
	Avg. (n=31)	16.23	18.75	47.72	49.8	0.07	8.49	0.005	
	DU2	1-43.7	9.7-32.3	24.8-103	22.8-84.1	0.041-0.17	2.25-18.5	0.002-0.022	
	Avg. (n=118)	15.46	19.47	49.06	47.16	0.08	6.98	0.008	
	DU1	1-40	13.2-33.3	29.1-103	30.7-84.4	0.04-0.16	2.25-17.2	0.003-0.02	
	Avg. (n=69)	18.36	20.59	54.3	54.05	0.08	6.19	0.009	
Yellow River Estuary		22.84	21.23	64.8	61.07	0.09	11.12	0.01	Liu et al. (2023)
Dongying Coast		22.5	21.6	70.2	66.4	0.12	12.8	na	Wu et al. (2022)
Laizhou Bay		19.06	20.3	55.98	60.1	0.11	11.72	0.038	Duan et al. (2021)
Southern Shandong Peninsula		23.1	25	71.1	64.3	0.08	11.4	0.032	Liu et al. (2015)
Coastal Shandong Peninsula		20	28.4	74.7	57.8	na	na	na	Li et al. (2013)
Element baseline in the soil of Shandong Peninsula		24	25.8	63.5	66	0.084	9.3	0.019	CNEMC, 1990

na, means no data.

2021), Southern Shandong Peninsula (Liu et al., 2015), and Coastal Shandong Peninsula (Li et al., 2013). The average concentrations of all metal(loid)s were below the element baseline in Shandong Peninsula soil (CNEMC, 1990).

Figure 4 illustrates the vertical profiles of the major and trace elements and the mean grain size (Mz) in the LZ01 sediment core. In addition to arsenic, all other metal(loid)s exhibited comparable distribution patterns, which were predominantly influenced by mean grain size. All metal(loid)s demonstrated the highest average concentrations in unit DU 4, which formed during the Holocene (Table 3).

4 Discussion

4.1 Assessment of sediment contamination

The results of the study, expressed as enrichment factors (EFs), are presented in Figure 5. The EFs of Cu, Pb, Zn, Cr, Cd, As, and Hg ranged from 0.06 to 2.34, 0.47 to 1.35, 0.62 to 1.47, 0.51 to 1.38, 0.62 to 2.02, 0.29 to 2.47, and 0.11 to 1.27, with mean values of 0.83, 0.92, 0.97, 0.92, 1.10, 0.92, 0.49, respectively (Table 4). The EF values decreased in the following order: Cd > Zn > Pb = Cr = As > Cu > Hg. The mean EF for all metal(loid)s was found to be below 1.5, indicating that these metal(loid)s were not subject to anthropogenic enrichment. The EF values for Cu, Cd, and As exceeded 1.5 in 2.68%, 11.26%, and 8.70% of the samples, respectively (Figures 5, 6A).

The I_{geo} values for Cu, Pb, Zn, Cr, Cd, As, and Hg in the sediments exhibited a range of -5.17 to 0.28, -2 to -0.22, -1.94 to 0.11, -2.12 to -0.23, -1.66 to 0.43, -2.63 to 0.41, and -4.15 to -0.37, with mean values of -1.33, -0.98, -0.93, -0.99, -0.76, -1.11, and -2.02, respectively (Table 4). The mean degree of pollution was highest for Cd, followed by Zn, Pb, Cr, As, Cu, and Hg. The mean I_{geo} values for all metal(loid)s were less than zero, indicating that the sediments were not contaminated by these metal(loid)s. The I_{geo} values for Cu, Zn, Cd, and As exceeded zero in 2.30%, 1.92%, 8.56%, and 5.93% of the samples, respectively (Figures 7, 6B).

The vertical distribution of E_r^i was similar to that of I_{geo} (Figure 8). Except for Cd and Hg, the concentrations of all the other metal(loid)s were considered to present a low potential ecological risk (E_r^i < 40) in all units (Table 4). For Cd, the sediments from units DU4, DU2, and DU1 were at moderate potential risk in a certain layer. For Hg, the sediments from units DU2 and DU1 were at moderate potential risk occasionally. The results of the comprehensive potential ecological risk index (E_R) showed that almost all metal(loid)s in the core sediments were at a low ecological risk (E_R < 105) (Figure 8). Only a few layers in DU4, DU2, and DU1 showed a moderate ecological risk, appearing in MIS1, MIS3-5, and MIS 6-7. Overall, the cumulative concentrations and potential ecological risk coefficients of the metal(loid)s in Laizhou Bay were low.

4.2 Source of the metal(loid)s

The Pearson's correlation coefficients between the concentrations of metal(loid)s (Cu, Pb, Zn, Cr, Cd, As, and Hg), selected major elements (Al, Ti, Mn and Fe), and Mz of the sediments are presented in Table 5. With the exception of As, Al

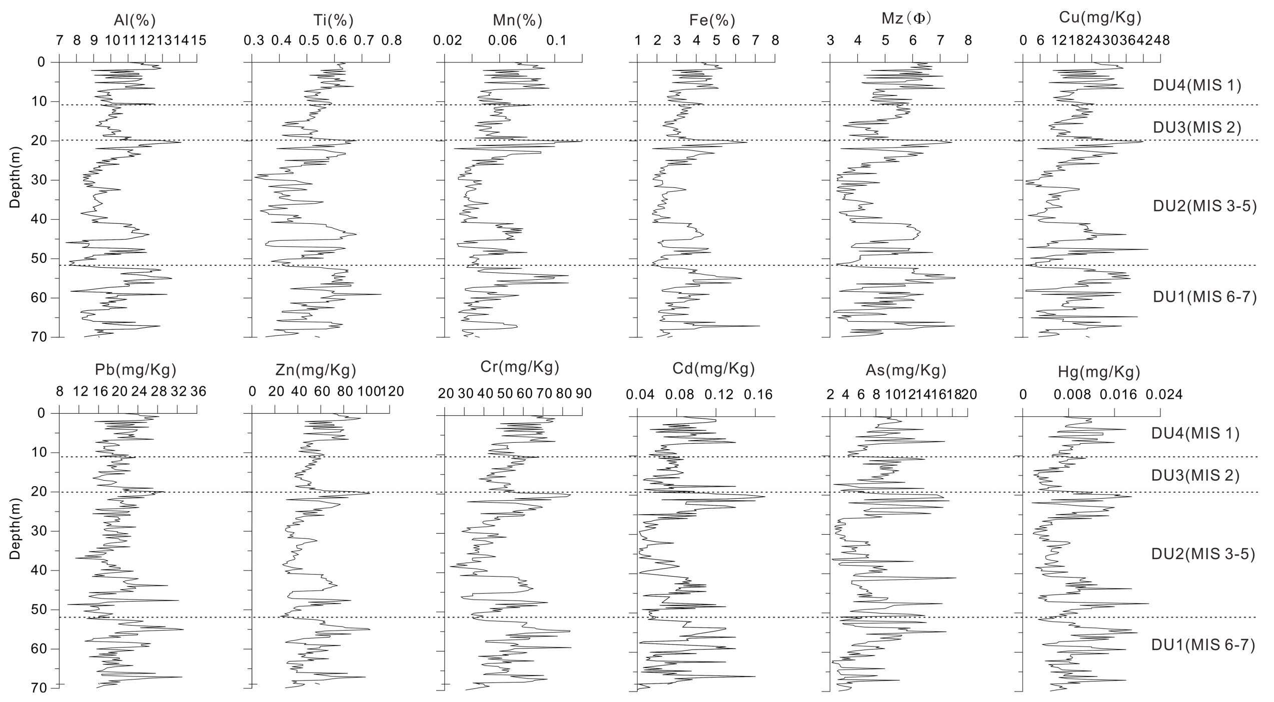

FIGURE 4
Vertical distribution of major and trace elements and mean grain size (Mz) in the core.

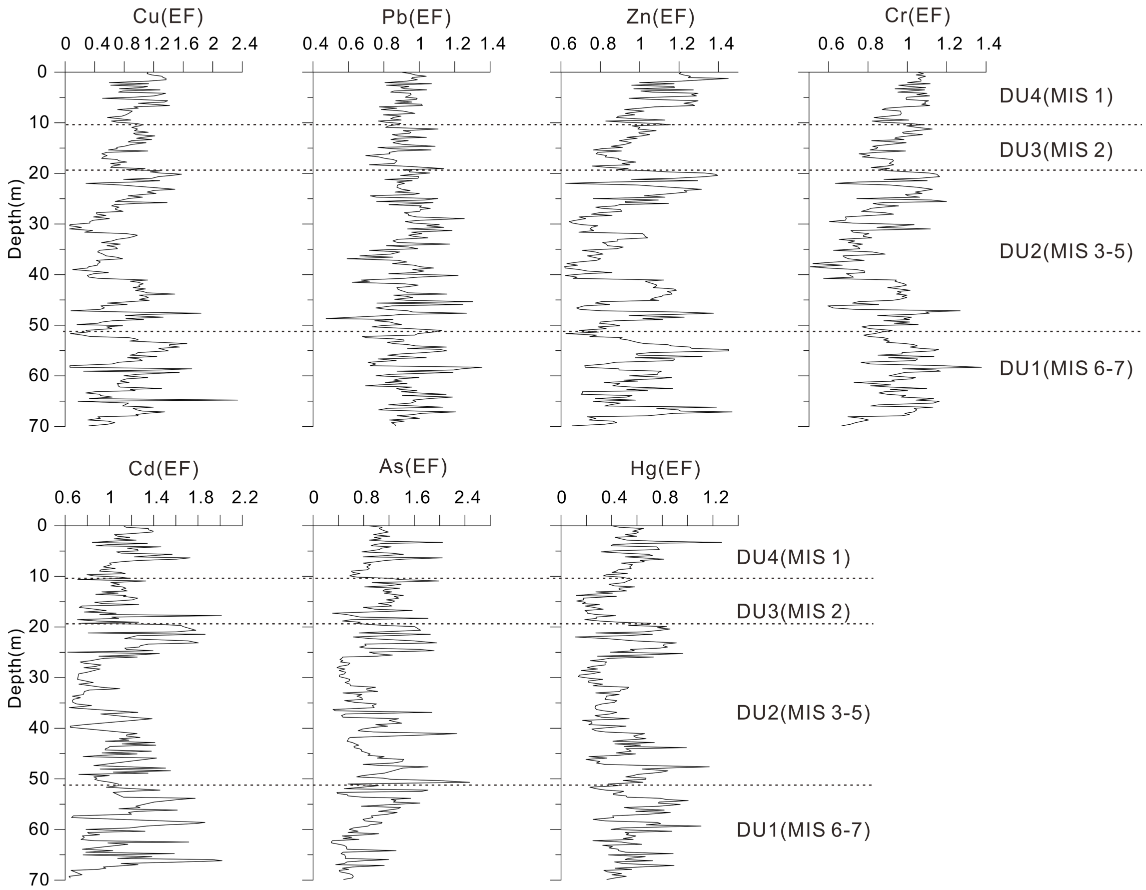

FIGURE 5
Vertical distributions of the EF values for metal(loid)s in the core.

demonstrated a strong correlation with the remaining elements (r = 0.709–0.939) and Mz (r = 0.861). Mz exhibited a moderate correlation with As and a positive correlation with the other elements. With the exception of As, all the remaining elements displayed a positive correlation with each other (1.0 > r ≥ 0.55).

In order to ascertain the sources of metal(loid)s in the environment, a principal components analysis (PCA) was conducted using the statistical software package SPSS. For the core sediments, the Kaiser-Meyer-Olkin (KMO) measure was 0.92, and the Bartlett's test yielded a value of 0, indicating that the heavy metal data in this study are suitable for PCA analysis (Waykar and Petare, 2016). The loadings are presented in Table 6. Two principal components with an eigenvalue greater than 0.9 were extracted, accounting for 82.46% of the total variance (Figure 9). Principal component 1 (PC1) contributed 74.67% of the total variance and included all metal(loid)s and Mz, with high loadings for Al (0.92), Ti (0.88), Mn (0.90), Fe (0.97), Cu (0.88), Pb (0.74), Zn (0.97), Cr (0.94), Cd (0.87), Hg (0.78), and Mz (0.89). This indicates that these metal (loid)s have the same sources. The significant positive correlations between Mz (Al, Ti, Mn, and Fe) and the metal(loid)s listed in Table 5 indicate that metal(loid)s are predominantly associated with fine terrigenous sediments (particularly clay minerals) via preferential

TABLE 4 Background values, EF, I_{geo}, and E_r^i values of metal(loid)s in the core LZ01.

Parameters	Cu	Pb	Zn	Cr	Cd	As	Hg
Mbackground[a] (mg/kg)	24	25.8	63.5	66	0.084	9.3	0.019
EF	0.06-2.34	0.47-1.35	0.62-1.47	0.51-1.38	0.62-2.02	0.29-2.47	0.11-1.27
	0.83	0.92	0.97	0.92	1.10	0.92	0.49
I_{geo}	-5.17-0.28	-2 to -0.22	-1.94-0.11	-2.12 to -0.23	-1.66-0.43	-2.63-0.41	-4.15 to -0.37
	-1.33	-0.98	-0.93	-0.99	-0.76	-1.11	-2.02
E_r^i	0.21-9.1	1.88-6.45	0.39-1.62	0.69-2.56	14.29-60.71	2.42-19.89	3.37-46.32
	3.62	3.86	0.83	1.56	28.28	7.79	16.97

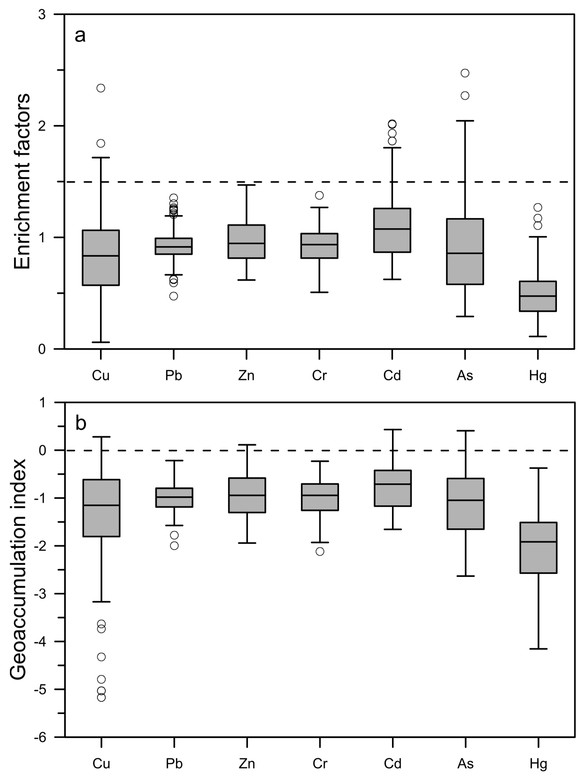

FIGURE 6
(A) Metal enrichment factors (EF) and **(B)** geoaccumulation indexes (I_{geo}) of metal(loid)s in the core sediments of the present study.

exchange and/or adsorption (Larrose et al., 2010). Aluminum oxide (Al_2O_3) is a product of continental differentiation and is relatively stable in the crust. Consequently, aluminum is regarded as a stable element in the transition from continents to oceans (Diagomanolin et al., 2004; Yuan et al., 2018), and is employed as an indicator of terrigenous components in the ocean and of terrigenous origin. The correlation between aluminum and metal(loid)s was found to be positive and moderate. In light of the combined results of EF and Igeo, it can be inferred that the metal(loid)s are derived primarily from crustal materials or natural weathering. Therefore, PC1 was identified as a natural source. PC2 accounted for 7.79% of the total variance, with a high loading for As (0.82). The EF and I_{geo} values of As exceeded 1.5 and zero in 8.70% and 5.93% of the samples, respectively. These occurrences were observed in a few layers within units DU 4, DU 2, and DU 1. In the context of historical times, it can be stated that there was no evidence of human activity. It can therefore be inferred that PC2 represents the change in sedimentary environment (Xiang et al., 2023).

4.3 Selection of elemental background values

The elemental background value refers to the content of chemical elements and compounds in soil that has not been influenced by human contamination. However, few accessible areas on Earth's surface have not been affected by human activities, and determining appropriate sampling sites is difficult. Therefore, the

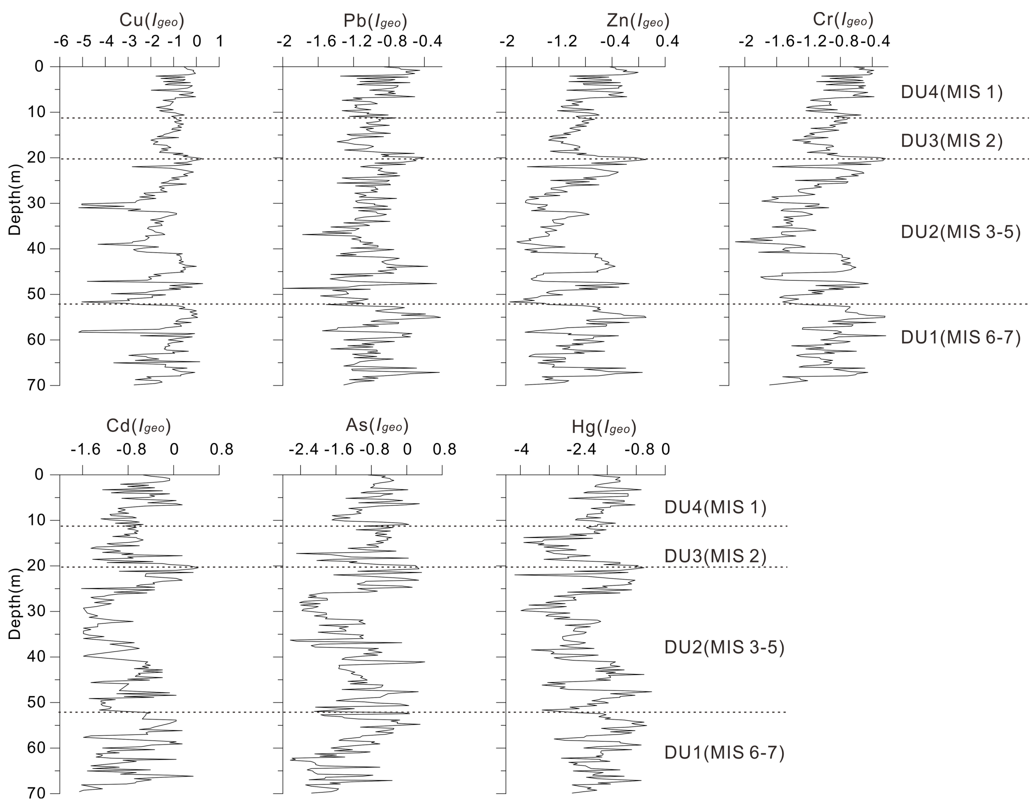

FIGURE 7
Vertical distributions of the I_{geo} values for metal(loid)s in the core.

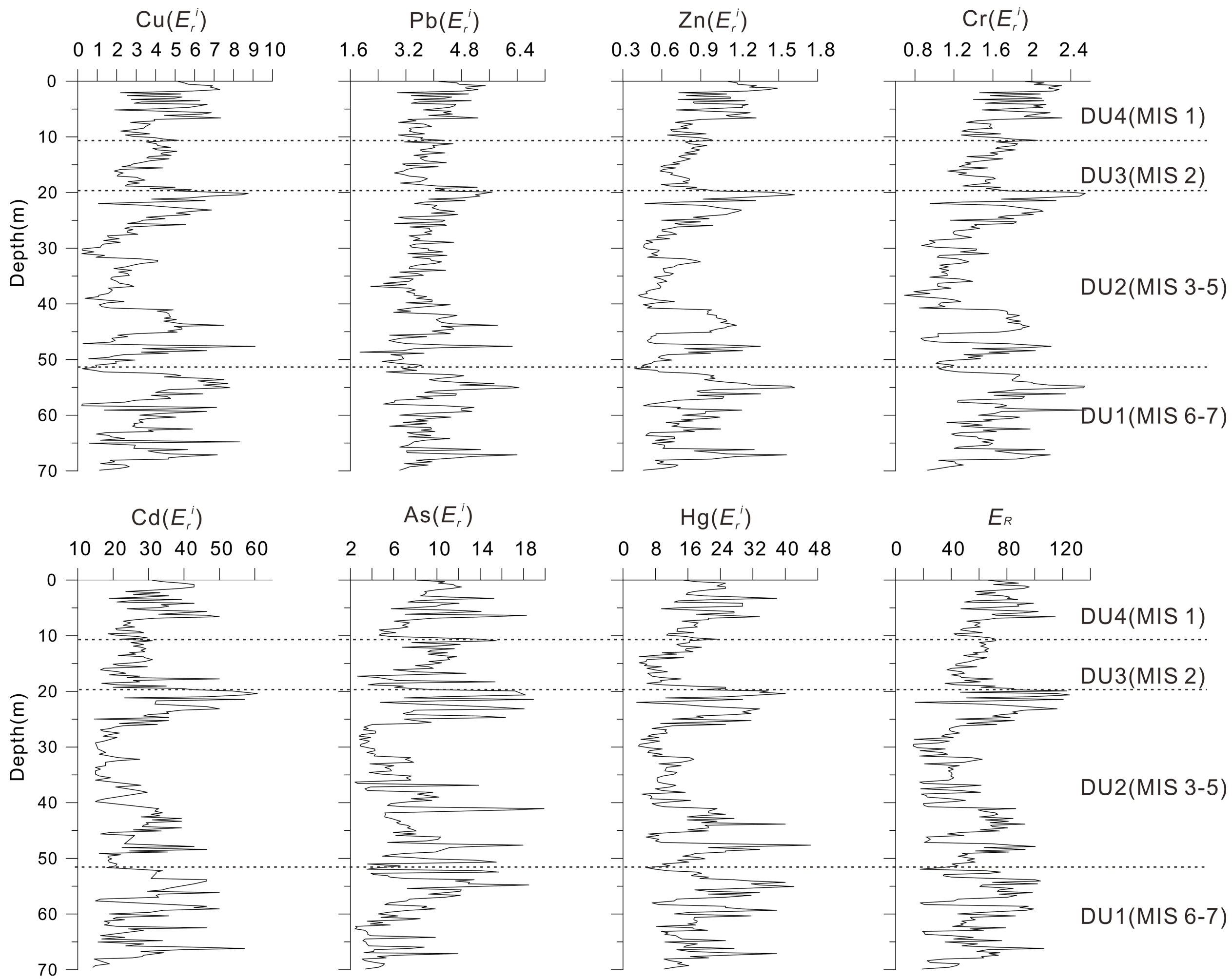

FIGURE 8
Vertical distributions of the E_r^i, and E_R values for metal(loid)s in the core.

TABLE 5 Pearson's correlation between elements and Mz (n= 261).

	Al	Ti	Mn	Fe	Cu	Pb	Zn	Cr	Cd	As	Hg	Mz
Al	1											
Ti	.801**	1										
Mn	.805**	.742**	1									
Fe	.925**	.827**	.903**	1								
Cu	.844**	.705**	.809**	.864**	1							
Pb	.709**	.550**	.641**	.713**	.679**	1						
Zn	.939**	.824**	.884**	.979**	.891**	.717**	1					
Cr	.867**	.908**	.840**	.923**	.792**	.669**	.921**	1				
Cd	.723**	.684**	.819**	.807**	.774**	.601**	.797**	.777**	1			
As	.446**	.375**	.602**	.564**	.471**	.252**	.510**	.465**	.528**	1		
Hg	.730**	.689**	.711**	.803**	.797**	.616**	.820**	.759**	.695**	.484**	1	
Mz	.861**	.806**	.838**	.887**	.815**	.618**	.882**	.844**	.728**	.491**	.708**	1

** means: Correlation is significant at the 0.01 level (two-tailed).

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TABLE 6 Extracted two principal components (PC1 and PC2) in core sediments.

Parameter	PC1	PC2
Al	0.92	-0.13
Ti	0.88	-0.12
Mn	0.90	0.16
Fe	0.97	0.01
Cu	0.88	-0.05
Pb	0.74	-0.42
Zn	0.97	-0.07
Cr	0.94	-0.08
Cd	0.87	0.15
As	0.52	0.82
Hg	0.78	0.00
Mz	0.89	0.01
Eigenvalues	8.96	0.94
Percentage of variances	74.67	7.79
Cumulative % eigenvectors	74.67	82.46

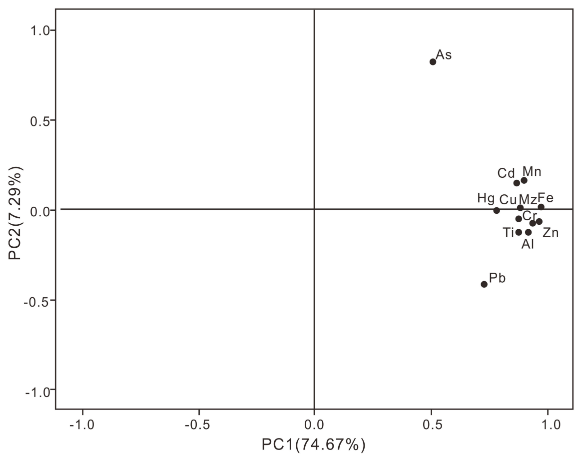

FIGURE 9
Principal component loading diagram for major and trace elements (Al, Ti, Mn, Fe, Cu, Pb, Zn, Cd, Cr, As, and Hg), and Mz in the core sediments.

use of drill core sediments from historical periods is a better approach for obtaining background elemental values. When assessing trace element pollution using surface sediments from the Laizhou Bay, the selection of different background values often leads to incomparable evaluation results (Xu et al., 2021; Zheng et al., 2022). In the present study, we used drill core sediments to determine the average content of trace elements in DU 4-2, including Cu (16.59 mg/kg), Pb (18.01 mg/kg), Zn (51.31 mg/kg), Cr (50.83 mg/kg), Cd (0.07 mg/kg), As (6.63 mg/kg), and Hg (0.01 mg/kg), which can be considered as background values for the Laizhou Bay region. The DU 4-2 unit was formed during the Early Holocene, when Laizhou Bay was submerged in seawater and the sea level was stable. The sediment source and depositional environment were similar to those of the present day, and no human activity occurred during this period. Therefore, the average values of trace elements in DU 4-2 can be considered as elemental background values.

4.4 Historical record of metal(loid)s

The sources and variations in heavy metal content in sediments are closely related to terrestrial inputs, sea-level changes, provenance shifts, and dynamic depositional environments (Wang, 2020). The DU 1 sedimentary unit formed during the MIS 6-7 period, which was a coastal-marine transitional setting. The rise of the Miao Island has impeded the exchange of water between the outer sea and the Bohai Sea. During periods of high sea level, the primary factors influencing the sedimentary environment in Laizhou Bay remain fluvial processes, with marine processes playing a secondary role. The study area is located at the terminal point of fluvial material transport, where sediment particles are relatively fine, likely dominated by sediments from the Yellow River, which exhibit higher concentrations of heavy metal elements. Entering Marine Isotope Stages (MIS) 3-5, the subsidence of the Miao Island uplift effectively ceased, resulting in a structural configuration of the Bohai Sea that is largely consistent with the present day. Sea level changes synchronized with the outer sea led to the formation of unit DU 2. The source of sediments in the study area may have shifted, now primarily consisting of near-source fluvial material from the southern shore of Laizhou Bay, characterized by coarser particle sizes and reduced concentrations of heavy metal elements in the sediments. The DU 3 sedimentary unit formed during the MIS2 period when the sea level was 120 m lower than it is today. The study area was exposed to the seabed and experienced fluvial deposition from small rivers and the Yellow River along the southern coast of Laizhou Bay (Yuan et al., 2023). The sediments were coarse grained. The heavy metal content in most of the sediments in the study area showed a strong correlation with grain size, indicating that metal(loid)s were mainly included/adsorbed into fine-grained sediments. Therefore, the heavy metal content of DU 3 was relatively low. During the Holocene, the sea level gradually increased and the study area was submerged by seawater. It was difficult for sediment from small rivers along the southern coast of Laizhou Bay to reach the study area, and the sediment in the borehole was mainly from the Yellow River with a fine grain size. The heavy metal content then began to increase.

5 Conclusion

The present study investigates the vertical distributions of major and trace elements and their pollution statuses in core sediments from Laizhou Bay, China. A general stratigraphic framework of the LZ01 core since the late Quaternary was established on the basis of sedimentary structures, sedimentary facies, grain size, and comparisons with other well-studied cores from adjacent areas. With the exception of arsenic, the distribution patterns of the remaining metal(loid)s were found to be similar and could be divided into four stages, which formed during the MIS 6-7, MIS 3-5, MIS 2, and MIS 1 periods. The highest average concentrations of metal(loid)s were observed in unit DU 4. The presence of multiple indicators indicated that there was no element enrichment or contamination in the core sediments, and that all metal(loid)s were of natural origin. The mean concentrations of the metal (loid)s in DU 4-2, which formed during the Early Holocene, can be used as reference values for background concentrations.

Data availability statement

The original contributions presented in the study are included in the article/supplementary material. Further inquiries can be directed to the corresponding authors.

Author contributions

LL: Conceptualization, Funding acquisition, Methodology, Writing – original draft. JG: Formal analysis, Investigation, Writing – original draft. SZ: Data curation, Resources, Writing – original draft. SL: Investigation, Software, Writing – original draft. DL: Investigation, Software, Writing – original draft. JZ: Validation, Visualization, Writing – original draft. XX: Software, Validation, Writing – original draft. BC: Conceptualization, Funding acquisition, Methodology, Writing – original draft. JQ: Formal analysis, Investigation, Writing – original draft.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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