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Research Article

Assessment of heavy metal pollution and ecological risk in the sediment of Cua Luc Bay, Quang Ninh Province

Huu Tuan Do[1]*

[1] Faculty of Environmental Sciences, VNU University of Science, Vietnam National University, Hanoi, 334 Nguyen Trai, Thanh Xuan, Hanoi, Vietnam; tuandh@vnu.edu.vn

*Correspondence: tuandh@vnu.edu.vn; Tel.: +84–2438584995

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Abstract: Heavy metals have big impacts on environmental quality and ecological risk. In this research, the I_{geo} accumulation index and ecological risk index (ERI) were used to assess the heavy metal pollution and ecological risk in the sediment of Cua Luc Bay, Quang Ninh Province. The results indicated that heavy metal concentrations in the study were almost lower than QCVN 43:2017/BTNMT. Only 3 monitored points, S1 (172.87 mg/kg), S3 (147.12 mg/kg), and S4 (115.54 mg/kg), have a light pollution level of Cu (108 mg/kg). The I_{geo} heavy metal accumulation index indicates that As (1.85), Cu (2.34), and Sb (1.42) are at a moderate level. While Se (3.65), Ag (3.58), and Sn (3.09) are at a high heavy metal level. As and Cu are two major factors posing ecological risk in the region (66.5%). However, the average ERI of all monitored points is 138, indicating that the ecological risk for heavy metals in the region is low. Despite having a low ecological risk for heavy metals in the region, it is necessary to strictly monitor heavy metals in sediment to manage them better in the future.

Keywords: Heavy metals; Ecological risk; Sediment; Heavy metals in sediment; Cua Luc Bay.

1. Introduction

Coastal bays play an important role in coastal ecosystems. With a typical mangrove forest ecosystem, the coastal bay is home to many species of marine animals that serve as food for humans. Coastal bays are also places where sediment is deposited and stored in mangrove forests. Therefore, sediments in coastal bays often contain heavy metals released from the mainland by rivers. The concern about heavy metals in sediments has been studied by many scientists for a long time. With their bioaccumulation in the food chain, heavy metals pose many potential risks to the ecosystem and human health. To assess heavy metal pollution in sediment, there are numerous methods such as Geo accumulation index, Ecological risk index, Enrichment Factor, Average pollution index, Pollution load index, Nemerow pollution index, Ecological risk factor [1]. In which, Geo accumulation index (I_{geo}), Ecological risk index (ERI) are more widely used [1]. There are numerous studies using Igeo to assess heavy metals in sediment such as in river sediment [2–5], urban sediment [6], coastal bays [7], reservoirs and dams [8, 9]. ERI is also an important method used to assess ecological risk for rivers [10], coastal [11], and wetland [12].

In Vietnam, heavy metals in sediment are also interesting research topics. The researches mainly focused on rivers such as rivers in Ho Chi Minh City [13], the Cau River [14], the Mekong River [15], the Nhue - Day River [16], lakes and dams [17]. However, research in coastal bays is still limited. Cua Luc Bay in Ha Long City is a place with an interaction between sea water flowing in from Ha Long Bay and river water from regional rivers such

as the Troi River and Dien Vong River. It also has mangrove forests that create an ideal environment for sediment deposition. Besides, the forest has sea foods as important sources of income for local people, especially species such as mangrove clams (Mud clam, Corrugate lucine), octopus, shrimp, crab, fish, etc. Therefore, assessing the level of heavy metal pollution and ecological risks in the region is important. The objectives of this study include assessing the level of heavy metal pollution and the ecological risk of heavy metals to the sedimentary environment in the area.

2. Methods

2.1. Samples collection

In the study, a suite of heavy metals was scrutinized, encompassing Arsenic (As), Selenium (Se), Chromium (Cr), Cobalt (Co), Nickel (Ni), Copper (Cu), Zinc (Zn), Molybdenum (Mo), Silver (Ag), Cadmium (Cd), Tin (Sn), Antimony (Sb), and Lead (Pb). Collection of sediment samples was executed in September 2023. Subsequent analytical procedures were conducted in strict adherence to the National Technical Regulation on Sediment Quality QCVN 43:2017/BTNMT.

Spatial delineation of sample provenance is elucidated in Table 1, while Figure 1 provides a graphical representation of the sampling sites, facilitating a comprehensive visual and quantitative assessment of the geographical distribution of the samples under investigation.

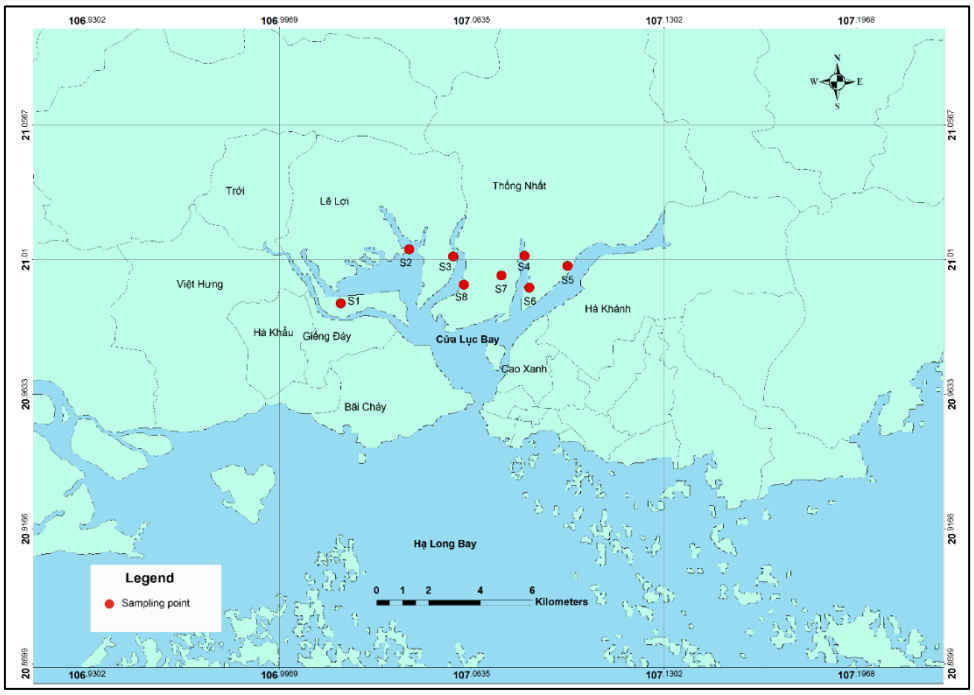

Figure 1. Location of sampling points.

Table 1. Coordinates of sediment sampling points.

Ord.	Sample Code	Longitude	Latitude
1.	S1	107.018116	20.994858
2.	S2	107.041819	21.013584
3.	S3	107.057094	21.011129
4.	S4	107.081856	21.011316
5.	S5	107.096709	21.007830
6.	S6	107.083500	21.000280
7.	S7	107.073800	21.004530
8.	S8	107.060800	21.001310

2.2. Methods

2.2.1. Ecological risk index (ERI)

To evaluate the potential ecological risk of heavy metal, ERI is used as an index method [18].

$$ERI = \sum RI = \sum Ti \times PI \quad (1)$$

where $PI = C_s/C_b$; PI is the pollution index, Cs is the observed metal concentration, Cb denotes the corresponding background values [19], Ti denotes the heavy metal's toxic-response factor, and RI stands for each heavy metal's potential ecological risk factor. The values of Cb and Ti were shown in the Table 2.

Table 2. Values of Cb and Ti [18–20].

Factor	As	Cr	Co	Ni	Cu	Zn	Cd	Pb
Cb (ppm)	2	35	11.6	18.6	14.3	52	0.102	17
Ti	10	2	5	5	5	1	30	5

After calculating, the ERI values were compared to the ERI levels: ERI < 150: low ecological risk; 150 ≤ ERI <300: moderate ecological risk; 300 ≤ ERI <600: considerable ecological risk; ERI ≥ 600 high ecological risk [18, 21]. Potential ecological risk factor for each metal: RI < 40: low risk; 40 ≤ RI < 80: moderate risk; 80 ≤ RI < 160 considerable; 160 ≤ RI < 320: high potential ecological risk; 320 ≤ RI: very high risk [21].

2.2.2. Geo Accumulation index (I_{geo})

Heavy metal pollution in soil and water sediments can be evaluated using the geo-accumulation index by [22]. The base two logarithms of the background metal concentration and the total metal concentration can be multiplied to find I_{geo} using the equation below.

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

where C_n is observed heavy metal concentration of samples; B_n is geo-chemical background concentration of heavy metals [19]; I_{geo} = 0-1: Low; I_{geo} = 1-3: Moderate; I_{geo} = 3-5: High [1].

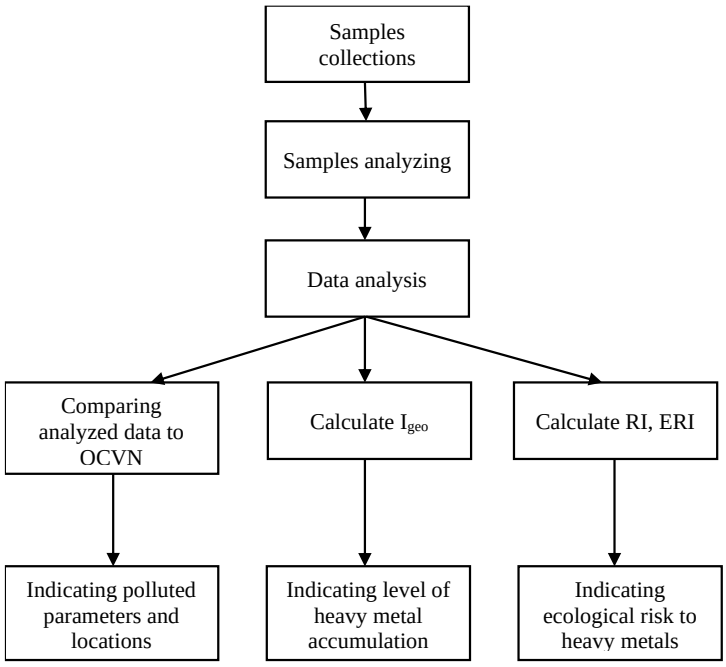

Figure 2. Research flowchart.

2.3. Statistical method

After analyzing samples, the results are subjected to basic and in-depth statistical processing using R statistical software (Figure 2).

3. Results and Discussion

3.1. Heavy metals in sediment

Analytical data presented in Table 3 indicate that arsenic (As) concentrations in the studied samples span a range from 8.38 to 11.73 mg/kg, mean concentration of 10.79 mg/kg. Notably, these concentrations remain below the permissible limit set by QCVN

43:2017/BTNMT, which is 41.6 mg/kg. Selenium (Se) exhibits a mean concentration of 1.57 mg/kg, with the observed concentrations varying between a minimum of 0.85 mg/kg and a maximum of 2.34 mg/kg. Chromium (Cr) concentrations in the environmental matrix exhibit a peak concentration of 28.05 mg/kg at sampling location S3, contrasting with the nadir of 10.02 mg/kg observed at point S4. All measured Cr concentrations were beneath the regulatory threshold of 160 mg/kg as prescribed by QCVN 43:2017/BTNMT.

Concentrations of cobalt (Co) and nickel (Ni) extend from 2.74 to 23.12 mg/kg and 9.17 to 45.96 mg/kg, respectively. The apex of Co and Ni concentrations was detected at sampling site S5, documenting concentrations of 23.12 mg/kg for Co and 45.96 mg/kg for Ni. Point S5's heightened metal concentrations are attributed to the influence of contaminants from the upstream sector of the Dien Vong River, an area that has been historically impacted by extensive coal mining activities.

Table 3. Desciptive statistics of heavy metals concentration (mg/kg).

Symbol	Mean	Standard Deviation	Minimum	Median	Maximum	QCVN 43:2017/BTNMT
As	10.79	1.17	8.38	11.39	11.73	41.6
Se	1.57	0.63	0.85	1.44	2.34	-
Cr	22.19	5.91	10.02	24.31	28.05	160
Co	8.70	7.20	2.74	5.87	23.12	-
Ni	20.41	13.40	9.17	15.01	45.96	-
Cu	108.27	46.35	38.96	119.03	172.87	108
Zn	62.26	11.32	48.78	61.16	83.06	271
Mo	2.24	0.81	0.96	2.40	3.08	-
Ag	0.99	0.72	0.23	0.73	2.19	-
Sn	32.04	8.26	19.84	34.47	44.31	-
Sb	1.24	0.34	0.85	1.20	1.66	-
Pb	17.42	4.06	9.59	16.99	22.35	112

In the context of this investigation, copper (Cu) has emerged as the most contaminated metal within the study area, with concentrations ranging from 38.96 mg/kg to an apex of 172.87 mg/kg. Notably, sampling points S1, S3, and S4 revealed Cu concentrations that exceed the regulatory standard of 108 mg/kg, with measured concentrations of 172.87 mg/kg, 147.12 mg/kg, and 115.54 mg/kg, respectively (Figure 3). These points of elevated Cu pollution are proximal to the industrial regions encompassing the communes of Gieng Day, Viet Hung, Le Loi, and Thong Nhat.

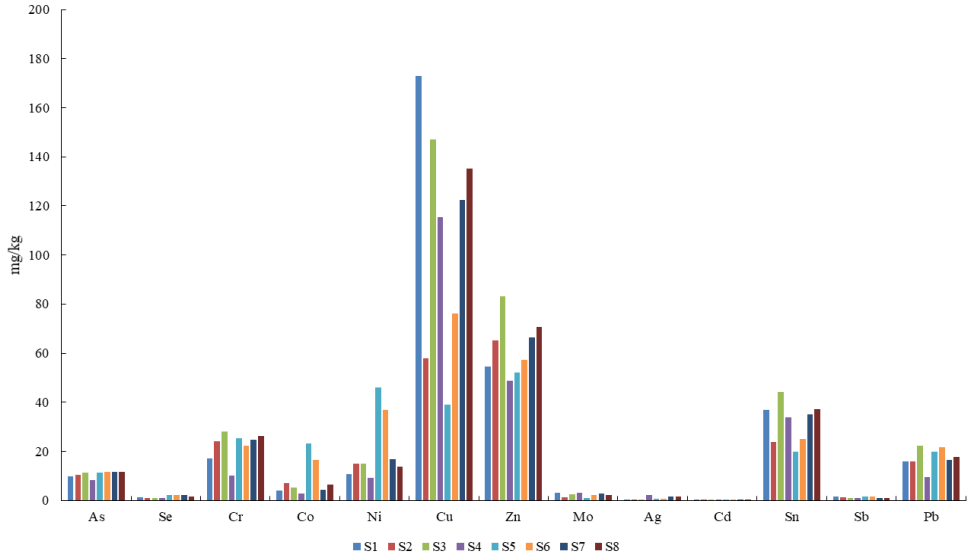

Figure 3. Concentration of heavy metals at sampling points in the study area.

Contrastingly, the concentrations of zinc (Zn) and lead (Pb) have been determined to be within acceptable limits. The average Zn concentration has been quantified at 62.26 mg/kg, which is considerably lower than the regulatory of 271 mg/kg as delineated by QCVN 43:2017/BTNMT. Similarly, the mean Pb concentration stands at 17.42 mg/kg, which is also below the prescribed standard of 172 mg/kg (Figure 4). This denotes a relatively lower level of pollution for these metals in the study areas.

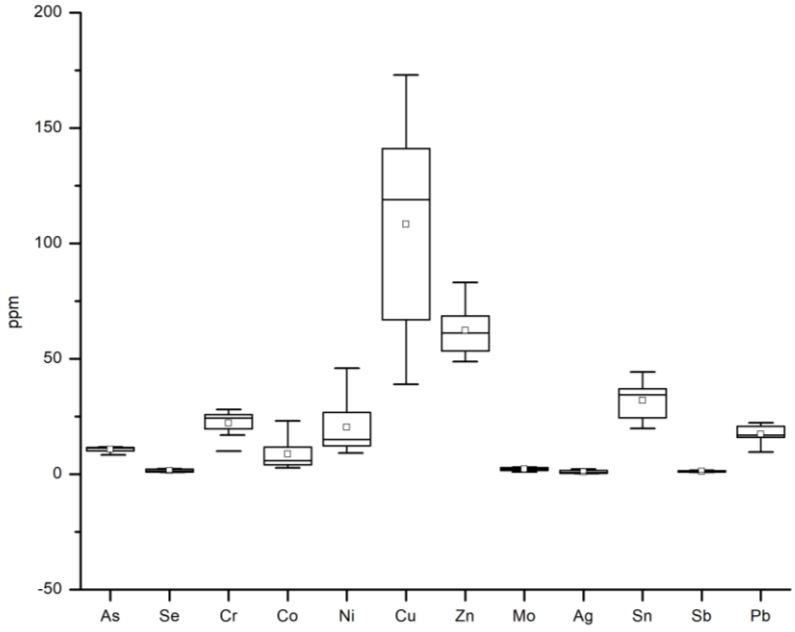

Figure 4. Concentration of heavy metals in sediment of the study area.

Comparing the monitored results with QCVN 43:2017/BTNMT reveals that most heavy metal parameters in the study area are below the regulated standards. Such findings suggest that despite the prevalence of industrial zones within the vicinity, the accumulation of heavy metals in the sediments of Cua Luc Bay remains at a low level.

3.2. Geo Accumulation index (I_{geo})

The geo-accumulation index (I_{geo}) was calculated to assess the pollution levels of various heavy metals in the study area, with the findings depicted in Figure 5. The I_{geo} values for Cr, Co, Ni, Zn, Mo, Cd, and Pb are indicative of low levels. Specifically, I_{geo} calculations for As spanned from 1.48 to 1.95, with an average of 1.85, positioning As within the moderate level category. Similarly, Cu presented I_{geo} values ranging from 0.86 to 3.01 with a mean value of 2.34, and Sb exhibited a range from 0.86 to 1.84 and an average of 1.42, both also classified as moderate levels.

Conversely, Se recorded higher I_{geo} values, from 2.77 to 4.23, with a mean of 3.65, indicating a high level of accumulation. Ag and Sn also fell into the high level category, with I_{geo} values for Ag ranging from 1.48 to 4.73 (mean 3.58) and for Sn ranging from 2.4 to 3.56 (mean 3.09). These elevated indices underscore a significant concern for the enrichment of these metals within the sedimentary environment of the study area.

Upon evaluating the concentrations of heavy metals within the scope of the regulatory QCVN 43:2017/BTNMT, it has been observed that only Cu exhibits a high I_{geo} value, indicating a considerable level of pollution. In contrast, other metals that are regulated under this standard, such as As, Cr, Zn, Cd, and Pb, are all characterized by low I_{geo} values, suggesting minimal geo-accumulation in the study area. However, for metals not explicitly regulated by QCVN 43:2017/BTNMT, such as Sb, Se, Ag, and Sn, there is a range from moderate to high I_{geo} values.

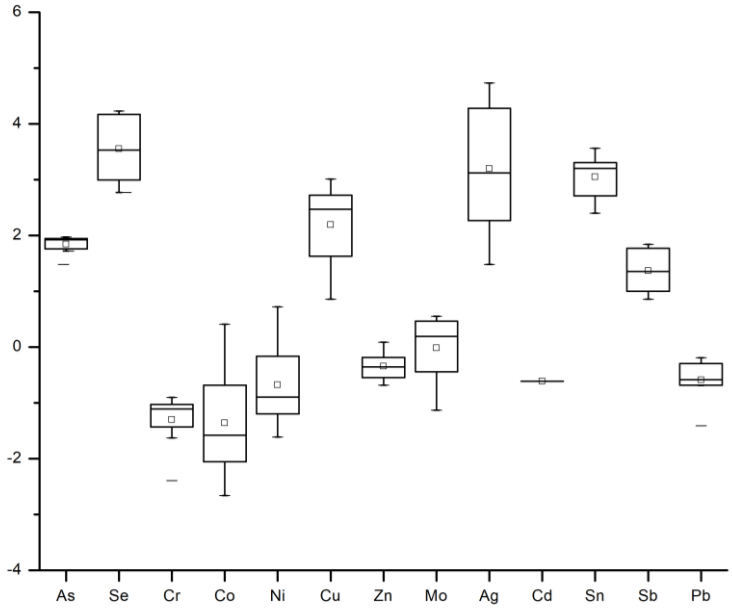

Figure 5. I_{geo} values of heavy metals.

3.3. Ecological risk of heavy metals

The potential ecological risk factor (RI), as tabulated in Table 4, indicates that arsenic (As) and copper (Cu) are the predominant contributors to the ecological risk in the region, together accounting for 66.5% of the total potential risk. The individual contributions of the heavy metals to the ecological risk of the region are: As constitutes 39% of the overall potential ecological risk, indicating it as the single most significant contributor. Cr represents a relatively minor portion, contributing 1% to the potential risk. Co accounts for 3% of the ecological risk, reflecting a lower level of concern in relation to As and Cu. Ni's contribution at 4%, to the risk. Cu is the second-largest contributor after As, responsible for 27% of the potential ecological risk. Zn with a contribution of 1%, Zn poses a relatively low risk under the current analysis. Cd often being present in lower concentrations, Cd represents a significant risk factor, contributing 21% due to its high toxicity. Pb contributes 4%, which is similar to Ni. These data underscore As and Cu as the primary metals of concern with respect to ecological risk within the study area. This suggests that remedial attention and mitigation strategies should prioritize the management of these metals to reduce potential ecological impacts.

Table 4. Heavy metal potential ecological risk factor (RI).

Symbol	S1	S2	S3	S4	S5	S6	S7	S8	Mean	Risk Factor
As	49.3	52.3	56.7	41.9	57.1	58.1	57.6	58.7	54.0	Moderate risk
Cr	1.0	1.4	1.6	0.6	1.4	1.3	1.4	1.5	1.3	Low risk
Co	1.8	3.1	2.2	1.2	10.0	7.1	1.8	2.8	3.7	Low risk
Ni	2.9	4.0	4.0	2.5	12.4	9.9	4.5	3.7	5.5	Low risk
Cu	60.4	20.2	51.4	40.4	13.6	26.7	42.8	47.2	37.9	Moderate risk
Zn	1.1	1.3	1.6	0.9	1.0	1.1	1.3	1.4	1.2	Low risk
Cd	<29.4	<29.4	<29.4	<29.4	<29.4	<29.4	<29.4	<29.4	<29.4	Low risk
Pb	4.7	4.7	6.6	2.8	5.8	6.4	4.8	5.2	5.1	Low risk

The assessment of the potential ecological risk factor (RI) for arsenic (As) across all monitored locations indicates that there is a uniform moderate risk level, with the RI values oscillating between 49.3 and 58.7. In terms of copper (Cu), sampling points S1, S3, S4, S7, and S8 are classified under a moderate risk category, while the remaining points, namely S2,

S5, and S6, are identified as having a low potential risk. For the other metals evaluated, namely Cr, Co, Ni, Zn, Cd, and Pb, the potential ecological risk is categorized as low across the board.

When the risk levels for Cua Luc Bay are placed in a comparative context with other coastal bays in the countries near Vietnam, as detailed in Table 5, a notable pattern emerges: The elements Cr, Co, Ni, Zn, and Pb are at a low risk in Cua Luc Bay as well as in the other surveyed coastal bays. Cua Luc Bay is distinguished by its low risk for cadmium Cd, whereas the comparative bays exhibit a range of potential risks, stretching from moderate to very high level.

Table 5. Heavy metal potential ecological risk in some coastal bays.

Symbol	Cua Luc Bay	Hangzhou Bay, China [23]	Ulsan Bay, South Korea [24]	Daya Bay, China [25]	Bay of Bengal Coast, Bangladesh [26]
As	Moderate risk	Low risk	Moderate risk	Low risk	Low risk
Cr	Low risk	Low risk	Low risk	Low risk	Low risk
Co	Low risk	Low risk	Low risk	-	-
Ni	Low risk	Low risk	Low risk	Low risk	-
Cu	Moderate risk	Low risk	Moderate risk	Low risk	-
Zn	Low risk	Low risk	Low risk	Low risk	-
Cd	Low risk	Moderate risk	High risk	Moderate risk	Very high risk
Pb	Low risk	Low risk	Low risk	Low risk	Low risk

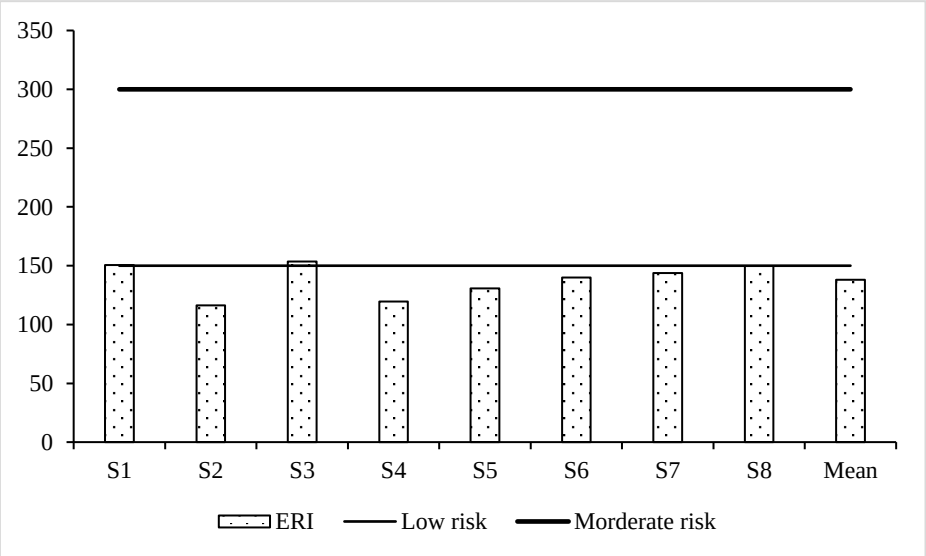

Figure 6. ERI values of sampling points.

The Ecological Risk Index (ERI) values delineated in Figure 6, spanning from 116.3 to 153.6, suggest variability in the potential ecological risk across different sampling points. Two specific points, S1 and S3, are classified as having moderate ecological risk, which is defined by an ERI between 150 and 300. All other points fall into the low ecological risk category, which indicates that their ERI values are below 150.

The mean ERI for all monitored points is calculated to be 138. This average positions the study area as a whole within the low ecological risk level for heavy metals. This assessment suggests that while there are specific areas of heightened concern (namely S1 and S3), the overall heavy metal contamination across the sampled locations does not pose a high ecological risk at this juncture. However, the areas with moderate risk warrant closer scrutiny and possible intervention to prevent any escalation in risk levels.

4. Conclusion

The study reveals that most heavy metal levels are below the threshold of QCVN 43:2017/BTNMT, with the exception of copper (Cu) at three points (S1, S3, and S4), which exceed the permissible levels. The Index of Geoaccumulation (I_{geo}) shows that As, Cu, and Sb have moderate accumulation levels, while selenium Se, Ag, and Sn are classified as having high accumulation levels. Arsenic and copper are the primary contributors to ecological risks in the area, accounting for 66.5% of the concern. However, the average Ecological Risk Index (ERI) for the area is 138, suggesting a low ecological risk from heavy metals overall.

Although the current ecological risk from heavy metals is low, the swift expansion of industrial areas could lead to greater risks in the future. It's crucial to maintain vigilant surveillance of heavy metals in the sediment. This is important to provide early warnings to local communities about the safety of consuming seafood from the mangrove forest.

The monitored samples for this research are limited. Deeper research with more samples is recommended to discover the potential risk of heavy metals in the region.

Author contribution statement: Constructing research idea: H.T.D.; Select research methods: H.T.D.; Data processing: H.T.D.; Sample analysis: H.T.D.; Take samples: H.T.D.; Writing original draft preparation: H.T.D.; Writing review and editing: H.T.D.

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

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