JOURNAL OF SCIENCE ON NATURAL RESOURCES AND ENVIRONMENT

ISSN 0866-7608

HANOI UNIVERSITY OF NATURAL RESOURCES AND ENVIRONMENT

No. 49

2023

JOURNAL OF SCIENCE ON NATURAL RESOURCES AND ENVIRONMENT

PUBLISHING LICENCE

No. 367/GP-BTTTT, dated September 29th 2023 of the Ministry of Information and Communications

PUBLISHED

Chau Anh Print Co.,Ltd

EDITORIAL OFFICE

No. 41 A Phu Dien Road, Phu Dien Ward, North-Tu Liem, Hanoi, Vietnam

Tel: 84-24-37645798, Fax: 84-24-38370597

Email: tapchikhtnmt@hunre.edu.vn

ISSUING SCOPE: Public Issue

DISTRIBUTOR: Department of Science Technology and International Relations

ISSN 0866 - 7608

CONTENTS
NO 49 * 2023

Science on Natural Resources and Environment 49 (2023) 24-32

Science on Natural Resources and Environment
Journal homepage: tapchikhtnmt.hunre.edu.vn

ASSESSMENT OF HEAVY METAL CONTAMINATION IN WATER AND SURFACE SEDIMENTS OF THE BA CHE RIVER ESTUARY, BAI TU LONG BAY, QUANG NINH PROVINCE

Dao Trung Thanh*, Nguyen Quoc Phi, Nguyen Thi Hong
Hanoi University of Mining and Geology, Vietnam

Received 27 October 2023; Accepted 20 December 2023

Abstract

Estuary sediments contain toxic heavy metals which can pollute coastal wetlands. Ba Che river estuary is a coastal wetland with an area of 2,844 ha, which is affected by wastes in Ba Che river water and aquacultures. In this study, the accumulation of heavy metals in the Ba Che river estuary was assessed based on the enrichment factor (EF), the geo-accumulation index (Igeo), and the ecological risk index (RI). Heavy metal concentrations were determined by the inductively coupled plasma mass spectrometry, after completing mineralization by microwave-assisted digestion. Results of the research, all heavy metals were detected in water samples with mean concentrations of As, Pb, Hg, Cd, Cr, and Zn in were range of 0.7-2.0; 0.7-2.2; 0.3-0.5; 0.2-0.6, 0.9-4.0; 4.3-13.9 µg/l; and in sediment were range of 4.01-11.24; 9.83-27.85; 0.42-0.46; 0.46-0.67; 4.73-18.25; and 42.49-129.17 mg/kg dry weight, respectively. Besides, the mean metal concentration in the water samples increased in the following order: Zn<Pb<Cu<As<Cd<Hg. Calculation of different ecological contamination factors showed that Hg is the primary contribution to ecological risk index (RI) origins from anthropogenic and urbanization sources.

Keywords: Heavy metals; Estuarine sediment; Ecological risk; Ba Che river estuary.

***Corresponding author. Email:** daotrungthanh@humg.edu.vn

1. Introduction

In estuarine areas, heavy metal contamination in water and sediment is increasingly serious, affecting the ecosystem and human health. A large amount of waste from manufacturing, shipping, and urbanization activities concentrates in the river mouth and then settles into sediment. Some contaminants that have been found in sediments include i) Synthetic organic compounds (polychlorinated biphenyls (PCBs) and industrial chemicals); ii) Polycyclic aromatic hydrocarbons (PAHs); iii) Heavy metals (As, Cd, Cr, Cu, Pb, Hg, Zn). In particular, the impact of heavy metals on aquatic ecosystems and humans is always a top concern for environmental researchers in the world and Vietnam [1].

The Ba Che river estuary is located in Quang Ninh's Bai Tu Long Bay. Its border to the North is close to Tien Yen, the West is close to 2 districts (Ba Che and Cam Pha), the East is close to Van Don districts, and the South is close to Cam Pha city. The area has undergone rapid economic development with the growth of industries like coal mining, shipping, aquaculture, and tourism. However, environmental protection measures have not kept pace with economic development, and this has resulted in a negative impact on the sedimentary environment. The impact on the sedimentary environment of the Ba Che river estuary is a result of the interaction between geological, hydrological, biological, and ecological processes that accompany human activities. In this study, tidal flat sediment samples were collected to facilitate the analysis of grain size and heavy metal content to obtain additional information and assess their impact on the environment.

2. Materials and methods

2.1. Study area

The water (TCVN 5998:1995 (ISO 5667-9: 1992)) and sediment (TCVN 6663-19:2015 (ISO 5667-19:2004)) samples were collected from three stations of coastal seawater and five stations of tidal flats at the Ba Che estuary are presented in Table 1 and Figure 1.

Table 1. Locations of sampling sites in the Ba Che river estuary intertidal zone

Code	Study location	Coordinate (VN2000, 3° zone)	
		X	Y
Seawater sample			
NB1	Voi Lon route, the South of Dong Rui, Tien Yen	2,342,967	461,852
NB2	Voi Lon route, near Hai Lang coast, Tien Yen	2,352,748	464,214
NB3	Near Mui Chua seaport	2,353,662	468,332
Sediment sample			
TT1	Ha Loan intertidal zone, Cong Hoa	2,342,535	463,918
TT2	The Southeast of Dong Rui intertidal zone	2,346,621	464,250
TT3	The North of Dai Xuyen intertidal zone	2,351,415	469,857
TT4	Hai Lang intertidal zone	2,353,855	464,949
TT5	Tien Lang intertidal zone	2,353,916	466,883

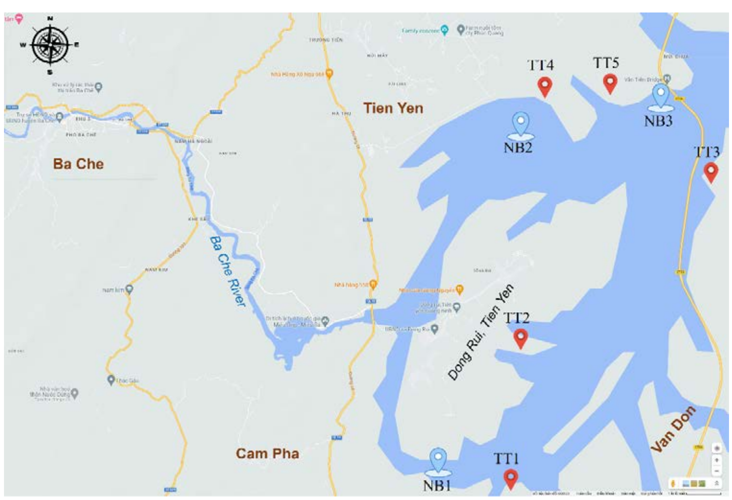

Figure 1: Location of sampling sites along the Ba Che river estuary intertidal zone

2.2. Sample preparation and instruments used

For seawater samples of this study, dissolved metal, and total metal samples were taken out of the refrigerator, put to room temperature, and analyzed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) according to US EPA Method 6020A [2].

The total concentrations of the metal ions (As, Pb, Hg, Cu, Cd, Zn, and Cr) in sediment samples were determined by ICP-MS after completing mineralization by microwave-assisted digestion. Therefore, 0.3 g of each sample was mixed with 9 ml of HNO_3, and 3 ml of HCl in a PFTE pressure vessel. After that, microwave-assisted digestion was performed through two steps in a microwave-accelerated reaction system. After the vessel cooled to room temperature, each digested sample was transferred into a PFTE beaker, then dissolved by 2 ml HNO_3 (30 %) and transferred by 2 % HNO_3 to rinse the vessel for three to five times into a 100 ml volumetric flask, and adjust the solution to the volume of 100 ml. Blank samples (without sediments) were prepared throughout the whole procedure.

2.3. Data processing and QA/QC

- Seawater quality data were averaged before statistical analysis and compared with the Local Technical Regulation on seawater quality (QCDP 2:2021/QN; QCVN 10-MT:2015/BTNMT). Sediment quality data were compared with the National Technical Regulation on sediment quality (QCVN 43:2017/BTNMT).

- Enrichment factor (*EF*) is usually used as a suitable means to discriminate between natural and anthropogenic sources of metal concentration in the sediment using the equation [3, 4]:

$$EF = \frac{C_n(sample)/C_{ref}(sample)}{B_n(background)/B_{ref}(background)} \quad (1)$$

where: $[C_n]$sample/$[C_{ref}]$sample is the sample concentration of metals in the analyzed sediment samples and $[B_n]$ background/$[C_{ref}]$background refers to the background value of the metal.

The average concentrations of metals in the sediment (background) for the selected research area are as follows: As = 11.2 mg/kg; Pb = 26.0 mg/kg; Hg = 0.065 mg/kg; Cd = 0.097 mg/kg; Cu = 22.6 mg/kg; Zn = 74.2 mg/kg [5, 6, 7]. Chromium (Cr) is considered a normalizing metal for three reasons: First, it is associated with fine to medium solid elements. Second, its geochemistry is comparable to that of many heavy metals. Finally, its natural concentration in the study area tends to be uniform [8].

The enrichment index of heavy metals in sediment is deduced in Table 2.

Table 2. Classify sediment quality according to the enrichment factor (EF) [4]

No.	Grade	Sediment quality
1	EF ≤ 2	Minorly enrichment
2	2 < EF ≤ 5	Moderately enrichment
3	5 < EF ≤ 20	Significantly enrichment
4	20 < EF ≤ 40	Highly enrichment
5	EF > 40	Greatly enrichment

- The Igeo relies on chemical data to evaluate the level of pollution. Geo-accumulation values are considered using the following equation [9]:

$$\text{Igeo} = log_2 \frac{C_n}{1,5B_n} \quad (2)$$

where: C_n is the considered contents of metal in the sample sediment and represents the chemical background concentration of the element in the background sample. Factor 1.5 is initiated to reduce the effects of probable dissimilarities in the background values which may be accredited to lithogenic effects [10].

The index of geo-accumulation values is deduced in Table 3.

Table 3. Classify sediment quality according to the Geo-accumulation index [4, 9]

Grade		**Sediment quality**
0	Igeo ≤ 0	Uncontaminated
1	0 < Igeo ≤ 1	Uncontaminated to moderately contaminated
2	1 < Igeo ≤ 2	Moderately contaminated
3	2 < Igeo ≤ 3	Moderately to heavily contaminated
4	3 < Igeo ≤ 4	Heavily contaminated
5	4 < Igeo ≤ 5	Heavily to extremely contaminated
6	Igeo > 5	Extremely contaminated

- Before assessing potential ecological risks, we must also define the degree of contamination (C_d) (Table 4). It represents the degree of contamination concerning heavy metals. This index can be computed via the following equations:

$$\mathrm{C_f^i} = \frac{\mathrm{C_D^i}}{\mathrm{C_R^i}} \quad (3)$$

$$\mathrm{C_d} = \sum_{i=1}^{n} \mathrm{C_f^i} \quad (4)$$

where: $\mathrm{C_D^i}$ is the measured concentration of the sample; $\mathrm{C_R^i}$ is the reference value according to Class I of the environmental quality standard for surface sediment (QCVN 43:2017/BTNMT); and $\mathrm{C_f^i}$ is the accumulating coefficient of metal (i).

Table 4. Classify sediment quality according to the degree of contamination [11]

Grade	**C_d**	**Sediment quality**
1	$C_d < 8$	Lowly contaminated
2	$8 \leq C_d \leq 16$	Mediumly contaminated
3	$16 \leq C_d \leq 32$	Significantly contaminated
4	$C_d \geq 32$	Highly contaminated

Based on the method developed by Hakanson (1980) [11], the potential ecological risk coefficient ($\mathrm{E_r^i}$) of a single metal and the potential ecological risk index (RI) of multimetal can be computed via the following equations:

$$\mathrm{E_r^i} = \mathrm{C_f^i}.\mathrm{T_r^i} \quad (5)$$

$$RI = \sum_{i=1}^{n} E_r^i \quad (6)$$

where: $\mathrm{E_r^i}$ is the potential ecological risk factor of each heavy metal (i) and $\mathrm{T_r^i}$ is the toxic factor of heavy metal (i), the values for Zn, Cu, Pb, As, Cd and Hg were 1, 5, 5, 10, 30 and 40, respectively [11].

The heavy metal contents in the sediment exceed the geochemical background concentrations and represent a multitude range of heavy metal toxicity in a particular specimen (Table 5) [12].

Table 5. Estimation of the ecological risk according to E_r^i and RI

Grade	E_r^i	RI	Ecological risk
1	$E_r^i < 40$	$RI < 94$	Lowly ecological risk
2	$40 \leq E_r^i < 80$	$94 \leq RI < 188$	Mediumly ecological risk
3	$80 \leq E_r^i < 160$	$188 \leq RI < 376$	Signifiantly ecological risk
4	$E_r^i \geq 160$	$RI \geq 376$	Highly ecological risk

3. Results and discussion

3.1. Heavy metal concentration in seawater

As shown in Figure 2, the concentrations of heavy metals (As, Pb, Hg, Cd, Cu, Zn) in four sampling periods (May 2020, Nov 2020, May 2021, and Nov 2021) met the standard of QCDP:2:2021/QN for seawater in Quang Ninh. Although the amounts of these heavy metals are below the allowable levels, their presence in seawater still has the potential to cause long-term health concerns. Thus, continuous monitoring of heavy metal concentrations in the seawater of the Ba Che river estuary is required to guarantee the safety of the estuary ecosystem.

The mean metal concentration in the water samples increased in the following order: Hg < Cd < Pb < As < Cu < Zn. Significant variations in the concentrations of metals were found among sites. However, overall, no clear trend could be observed for the three sites.

3.2. Heavy metal concentration in sediment

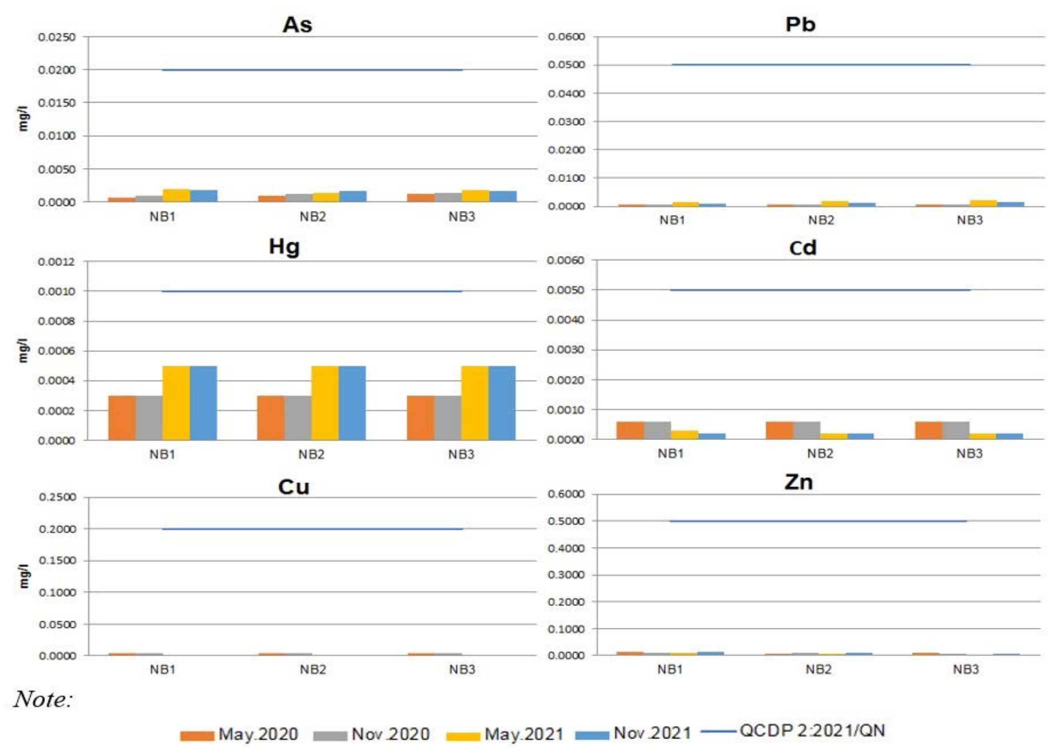

Figure 2: Station wise heavy metal concentration in samples of seawater according to location and sampling time

As shown in Figure 3, all of the heavy metal concentrations in the sediment were lower than the allowed standard (QCVN 43:2017/BTNMT). The As concentrations in the sediment ranged from 4.01 to 11.24 mg/kg, Pb ranged from 9.83 to 27.85 mg/kg, Hg ranged from 0.42 to 0.46 mg/kg, Cd ranged from 0.46 to 0.67 mg/kg, Cr ranged from 4.73 to 18.25 mg/kg, Zn ranged from 42.49 to 129.17 mg/kg. The concentration of metals in decreasing order from the highest to lowest was as follows: Zn > Pb > Cr > As > Cd > Hg.

In this study, the results of analyzing the content of heavy metals in sediment did not exceed the allowed limit, however, they were higher than the results of the previous study (Nguyen Thi Thuc Anh et al., 2006) [13], except for Pb and Hg. It has been corroborated that the content of heavy metals in the sediments of the study area is increasing and is likely to impact benthic organisms due to sediment disturbance.

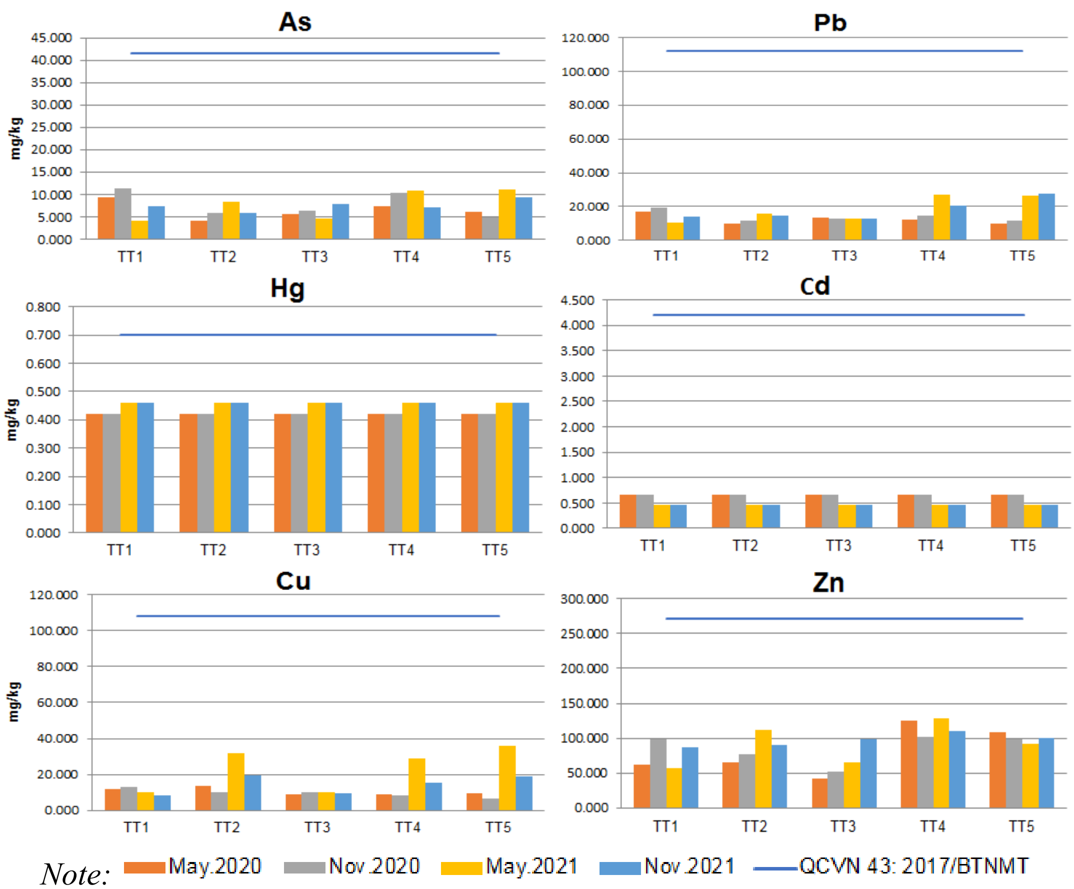

Figure 3: Station-wise heavy metal concentration in samples of sediment according to location and sampling time

The EF values were calculated according to formula (1) in Section 2.3, which found moderate to significant As, Pb, Cu, and Zn enrichment and significant to very high Hg and Cd contamination. In addition, the study showed heavy metals suggesting similar or possibly identical sources for these elements, presumably from local untreated wastewater. Atmospheric sources, such as natural gas, and oil and gas combustion should also be considered.

Table 6. Mean value of enrichment factor (EF) of selected heavy metals at different times

Date	As	Pb	Hg	Cd	Cu	Zn	Sediment quality
May-2020	3.68	3.25	45.51	48.65	3.47	7.06	Moderately to great enrichment
Nov-2020	4.12	3.36	43.03	45.99	2.80	7.21	Moderately to great enrichment
May-2021	3.46	3.53	33.18	22.24	5.10	5.99	Moderately to high enrichment
Nov-2021	4.83	5.26	50.19	33.63	4.63	9.45	Moderately to great enrichment

Results of *Igeo* values of the tidal flat sediment heavy metals are given in Table 7. Based on our classification results, the study area may be considered moderately to heavily contaminated with Hg and Cd ($1 < Igeo \leq 3$). This might be due to the input of the mining industry and aquaculture activities. In addition, a lower degree of contamination was found in the sediments by Zn (at TT4) and Cu (at TT5). There was no contamination from As, Pb, Cu, and Zn in the sediments (*Igeo* < 0).

Table 7. Description of Geo-Accumulation Index (Igeo) of selected heavy metals at different sites

Date	Symbol	Igeo					
		As	Pb	Hg	Cd	Cu	Zn
May-2020	TT1	-0.839	-1.216	2.107	2.203	-1.530	-0.841
	TT2	-2.067	-1.988	2.107	2.203	-1.334	-0.778
	TT3	-1.616	-1.502	2.107	2.203	-1.891	-1.389
	TT4	-1.177	-1.677	2.107	2.203	-1.913	0.176
	TT5	-1.488	-1.952	2.107	2.203	-1.846	-0.030
Nov-2020	TT1	-0.580	-1.019	2.107	2.203	-1.359	-0.166
	TT2	-1.552	-1.752	2.107	2.203	-1.701	-0.523
	TT3	-1.424	-1.629	2.107	2.203	-1.746	-1.098
	TT4	-0.706	-1.427	2.107	2.203	-1.996	-0.123
	TT5	-1.816	-1.731	2.107	2.203	-2.405	-0.180
May-2020	TT1	-1.990	-1.901	2.238	1.661	-1.707	-0.956
	TT2	-1.002	-1.309	2.238	1.661	-0.083	-0.003
	TT3	-1.878	-1.583	2.238	1.661	-1.707	-0.758
	TT4	-0.636	-0.542	2.238	1.661	-0.228	0.215
	TT5	-0.584	-0.555	2.238	1.661	0.088	-0.281
Nov-2021	TT1	-1.193	-1.447	2.238	1.661	-1.967	-0.361
	TT2	-1.502	-1.385	2.238	1.661	-0.811	-0.317
	TT3	-1.109	-1.565	2.238	1.661	-1.840	-0.170
	TT4	-1.236	-0.910	2.238	1.661	-1.111	-0.025
	TT5	-0.839	-0.486	2.238	1.661	-0.851	-0.155

The contamination factor (C_f^i) for individual metals and the degree of contamination (C_d) are presented in Table 8. The assessment of the integrated contamination degree of sediments is based on the degree of contamination (C_d). The ranges of C_d were 1.42-1.67, indicating low contamination of the sediment environment.

Table 8. Results of contamination factor (Cd) of selected heavy metals at different sites

	As	Pb	Hg	Cd	Cu	Zn	C_d	Sediment quality
C_f^i	0.16-0.19	0.11-0.17	0.60-0.66	0.11-0.16	0.09-0.22	0.30-0.36	1.42-1.67	Lowly contaminated

The results of the potential ecological risk factor and the potential ecological risk index (*RI*) are presented in Table 9. The order of *RI* in sediments was in the following ascending order of Zn < Pb < Cu < As < Cd < Hg and the potential ecological risk for a single metal was the low-risk group. Combining the potential ecological risk index of individual metals (Table 9) with its grade classifications, every single metal showed low potential ecological risk.

Table 9. Results of ecological risk factor (RI) of selected heavy metals at different sites

	As	Pb	Hg	Cd	Cu	Zn	*RI*	Ecological risk
E_r^i	1.55-1.89	0.56-0.83	24.0-26.29	3.29-4.79	0.45-1.09	0.30-0.36	31.69-33.71	Lowly ecological risk

In summary, there are no signs of contamination and ecological risks of heavy metals in the tidal flat sediments of the Ba Che river estuary. However, there is still a need for measures to reduce major contributors of heavy metals such as Hg and Cd because of their high toxicity to the ecosystem.

4. Conclusion

Analysis results show that coastal sea waters and tidal flat sediments at the Ba Che river mouth have not been contaminated with heavy metals. However, the results of calculating the geochemical accumulation index showed that the metals Hg and Cd were contaminated at a moderate to heavy grade. Heavy metal content in sediment tends to increase over time and is evenly distributed at sampling locations.

Evaluation of the enrichment factor (*EF*) and ecological risk (*RI*) shows that Hg and Cd have high to great enrichment grades, with Hg having the largest ecological risk contribution. The average value of the potential ecological risk index of metals arranged in ascending order from Zn < Pb < Cu < As < Cd <Hg.

The sedimentary environment in the Ba Che river estuary is moderate to heavily contaminated nearshore. The highest concentrations of heavy metal in sediments near the coast come from coal mining, shipping, aquaculture, and river inflows where there is a high content of silt and clay fraction.

Acknowledgments: This research was funded by the project with the title of *"Research impact assessment of As, Pb, Hg, and Cd contamination in Ba Che river water on Dong Rui aquaculture area, Bai Tu Long Bay, Quang Ninh"*. Code T23-36.

REFERENCES

[1]. Saha P. K. and Hossain M. D., (2011). *Assessment of heavy metal contamination and sediment quality in the Buriganga River, Bangladesh*. 2nd International Conference on Environmental Science and Technology, 384.

[2]. Tessier P. G. C. Campbell and Bisson M., (1979). *Sequential extraction procedure for the speciation of particulate trace metals.* Analytical Chemistry, Vol. 51, 844.

[3]. Kehrig H. A., Pinto, F. N., Moreira I., Malm O., (2003). *Heavy metals and methylmercury in a tropical coastal estuary and mangrove in Brazil*. Organic Geochemistry, 34, 661.

[4]. Maurizio Barbieri, Angela Nigro, Giuseppe Sappa (2015). *Soil contamination evaluation by Enrichment Factor (EF) and Geoaccumulation Index (Igeo)*. Senses Sci, 2(3), 94.

[5]. Quy, T. D., Tue, N. T., and Nhuan, M. T., (2012). *Spatial distribution of trace elements in surface sediments of Tien Yen Bay, northeast Vietnam.* Vietnam Journal of Earth Sciences, 34(1), 10-17.

[6]. Krauskopf K. B., (1979). *Introduction to Geochemistry.* McGraw Hill, New York.

[7]. Zhang, Lulu, Liu, Jingling (2014). *In situ relationships between spatial-temporal variations in potential ecological risk indexes for metals and the short-term effects on periphyton in a macrophyte-dominated lake: A comparison of structural and functional metrics*. Ecotoxicology, 23(4), 553.

[8] McMurtry G. M., Wiltshire J. C. and Kauahikaua J. P., (1995). *Heavy Metal Anomalies in Coastal Sediments of Oahu, Hawaii*. Pacific Science. 49: 452-470.

[9]. Muller G., (1969). *Index of Geo-accumulation in sediment of the Rhine River.* GEO Journal, Vol. 2, No. 3, 108.

[10]. Loska K., Wiechula D. and Korus I., (2004). *Metal contamination of farming soils affected by industry*. Environmental International, 30, 159.

[11]. Hakanson L., (1980). *An ecological risk index for aquatic pollution control. A sedimentological approach*. Water Research, Vol. 14, No. 8, 975.

[12]. Liu Z. J., Li P. Y., Zhang X. L., Li P., Zhu L. H. (2012). *Regional distribution and ecological risk evaluation of heavy metals in surface sediments from coastal wetlands of the Yellow River delta*. Environ Sci 33(4), 1182.

[13]. Nguyen, T. T. A., & Nguyen, K. G. (2006). *Current status of heavy metal contamination in estuary sediments in Tien Yen-Ha Coi Gulf, Quang Ninh*. Journal of Geology, 293(3-4), 1-10.