Vietnam Journal of Science and Technology ***56*** *(2C) (2018) 72-79*

INVESTIGATION AND ECOLOGICAL RISK ASSESSMENT OF Pb, As AND Hg IN SEDIMENT OF TAM GIANG-CAU HAI LAGOON, THUA THIEN HUE PROVINCE

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Received: 10 May 2018; Accepted for publication: 21 August 2018

ABSTRACT

Tam Giang - Cau Hai lagoon plays an important role in coastal ecosystems of Thua Thien Hue Province. The present study aims to determine three toxic elements (Pb, As, Hg) in the surface sediment and to assess the ecological risk of the selected metal in this area. Sediment samples and water quality were collected at 9 stations in rainy and dry seasons. Toxic metals were determined following the USEPA methods 3050A for measuring by atomic absorption spectrophotometer. Concentrations of Hg, Pb and As in the study area were in the range of 0-2.64 mg/kg, 4.83-22.13 mg/kg and 1.18-6.24 mg/kg, respectively. The results showed that concentration of Hg in sediment of most sampling sites were exceeded the National Technical Regulation on Sediment Quality (QCVN 43:2012/BTNMT), while Pb and As were below the regulated level. Ecological risk assessment presented that investigated metals posed medium to high risk to ecology. The estimated ecological risk index (ERI) ranged from 43.9 to 582.9 with the order of Hg>As>Pb. The highest ecological risk was found at the stations closed to the Thuan An inlet and ship construction area.

Keywords: Tam Giang – Cau Hai lagoon, ecological risk assessment, toxic metals.

1. INTRODUCTION

The existence of heavy metals in the lagoon sediments are caused by both natural and anthropogenic sources. In past decades, the increasing of human development activities has been accelerated the deliveries of metals into the coastal lagoons. Estefan m. Fonseca, 2011 suggested that high concentrations of heavy metals in the urban runoff sediments can be considered an important sources of heavy metal to the lagoon [1]. For example, high concentration of Zn and Ni found in Lagos lagoon was determined from industrial areas [2]. The accumulation of toxic metals in the sediment is the major threats to the organisms in aquatic ecosystems [3]. Several studies showed that the high concentration of the heavy metals in the sediments such as Hg, Cd, Pb were the causes of negative effect to aquatic organisms by direct or indirect pathways.

Therefore, the investigation of toxic metals distribution and ecological risk assessment is very important to understand the impacts into ecosystems.

In Vietnam, the background data of heavy metals in the lagoon sediments still limited, and ecological risk assessment for Tam Giang-Cau Hai lagoon has not documented. Recently, Minh VV et al., 2014 depicted that high concetration of heavy metals in the sediments of some estuaries of Central of Vietnam, in which highest concentration of Pb was determined in the sediment of Thuan An estuary, is a part of Tam Giang-Cau Hai lagoon [4]. Therefore, this study focused to investigate the concentration of heavy metals and assessment the ecological risk for the Sam-Chuon area an important part of Tam Giang-Cau Hai lagoon and tend to supply the background data for the lagoon systems in Vietnam.

2. MATERIALS AND METHODS

2.1. Sediment sampling and preservation

Surface sediments and waters were sampled at the 9 stations (M1 to M9) in the Sam Chuon areas of Tam Giang-Cau Hai lagoon (Figure 1). The water quality parameters such as DO, pH, TDS, EC and salinity were measured by field instrument (Horiba-22, Japan). Surface sediments were sampled by the sediment core sampler (Cole-Palmer), then wrapped and stored in cool bag, moving to laboratory in the same day. 1,5 litter of water at each station was sampled and contained in cleaned PET bottles for measure BOD5 and COD. Sampling was conducted three times in March, May and August of 2016.

2.2. Samples treatment

Sediments samples were treated following the guidline of USEPA, method 3050A for As, Hg and Pb measured by AAS (Atomic Absorption Spectrophotometer). Sediment after freeze dried was crushed and sieved by size 0.5 mm. Weighing about 2 g of sediment and digested by acid solution in the teflon bottles for analysis [5].

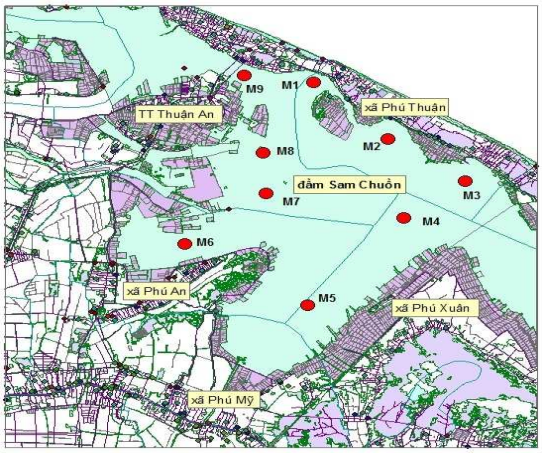

Figure 1. The diagram of sampling sites.

2.3. Ecological risk assessment

** Determination of contamination factor-CF*

Contamination factor was used to evaluate the contamination status of sediment, it was calculated following the equation presented by Hakanson as below:

$$CF=\frac{C_{Me}}{C_B} \quad (1)$$

where C_{Me} is the concentration of heavy metals; C_B is the background concentration (used the data by Turekian, 1961) as Table 1.

Table 1. Background concentration of heavy metals in sediment (mg/kg).

Metals	As	Hg	Pb	Fe
C_B	1,9	0,08	15	29.600

* *Enrichment Factor – EF:* Enrichment factor (EF) was calculated based on the equation (2) showed by Silva, 2011:

$$\mathbf{EF}=\frac{(C_{Me}/C_{Fe})Sample}{(C_{Me}/C_{Fe})Background} \quad (2)$$

* *Geoaccumulation Index - I_{geo}*

$$I_{geo} = \log_2\left(\frac{C^i}{1{,}5 \times C_n^i}\right) = \log_2\left(\frac{C_F}{1{,}5}\right) \quad (3)$$

where: C_n is the concentration of heavy metals in sediments; B_n is background concentration of metals.

* *Ecological Risk – ER:* ER presents the ecological risk of each metal was calculated follow the equation:

$$ER = T_R^i \frac{C^i}{C_o^i} = T_R^i \times C_F \quad (4)$$

Where: T^i_R: toxic level; C^i: concentration of heavy metals in sediment; C^i_o: background concentration.

* *Pollution Load Index - PLI*

$$PLI = \sqrt[n]{(CF_1 \times CF_2 \times \cdots \times CF_n)} \quad (5)$$

* *Ecological Risk Index - ERI* (Radhouan El Zrelli, 2015):

$$ERI = \sum_{i=1}^{n} ER_i \quad (6)$$

where: ER is ecological risk of each metal; n is number of metals.

3. RESULTS AND DISCUSSION

3.1. Characteristic of water quality at Sam Chuon area, Tam giang – Cau Hai lagoon

Water quality parameters play a major role in the accumulation and resuspending of heavy metals in the sediments such as pH, DO, EC, e.g. Table 2 shows the value of the water and sediment parameters at the sampling sites. In general, there was no significant difference on water quality at the sampling sites, most of the parameters was under the National Technical Regulation of Vietnam on marine water quality for aquaculture activities at the coastal zone (QCVN 10 MT:2015/BTNMT). These data are also of not difference with the previous studies at Tam Giang – Cau Hai lagoon [6], and coincided with the results conducted at the Butrinti and Ebrie lagoons [7].

Table 2. Physio-chemical characteristics in the water and sediment of Sam Chuon area, Tam Giang - Cau Hai lagoon.

Site		pH	DO (mg/L)	Sal‰ (ppt)	TDS (mg/L)	BOD_5 (mg/L)	COD (mg/L)	LOI (%) in sediment
M1	Min-Max	7.9-8.3	4.9–6.7	13.0-24.3	18-26	1.5-1.6	9.1-11.1	5.5-14.6
	Avg± SD	8.1±0.5	5.8±1.3	18.1±5.7	22±10	1.6±0.1	10.4±2.6	13.7±4.3
M2	Min-Max	7.9-9.0	4.5-7.3	17.4-23	18-26	1.7-2.1	10.5-14.0	3.5–11.9
	Avg± SD	8.4±1.4	5.9±2.0	20.4±7.0	22±10	1.9±0.3	12.5±4.5	8.6±4.5
M3	Min-Max	8.2–8.8	6.5-6.6	19.2-23.0	19-27	1.5–3.7	11.7–13.3	2.3–9.3
	Avg± SD	8.5±0.8	6.6±0.8	20.6±5.3	23±10	2.6±1.5	12.5±2.1	5.4±3.6
M4	Min-Max	8.4-8.7	5.2-6.7	20.0-23.6	20-26	1.4-4.7	10.7-15.8	4.6–9.2
	Avg± SD	8.6±0.4	6.0±1.2	21.6±4.5	23±8	3.0±2.3	13.9±7.0	7.7±2.6
M5	Min-Max	8.6-10.5	4.5–8.4	18.6–2.,6	19-25	1.6–5.8	12.2–16.3	2.6–10.2
	Avg±SD	9.9±2.7	6.5±2,8	21.5±6.4	22±9	3.7±3.0	14.5±5.2	7.0±4.0
M6	Min-Max	8.6–10.8	4.0–6.7	20.8–23	20-26	1.1–4.4	11.4–17.6	8.0–13.2
	Avg±SD	9.4±3.0	5.3±1.9	21.9±3.2	23±8	2.1±0.7	13.7±8.5	9.7±3.0
M7	Min-Max	9.9-10.4	4.6-6.7	17.7-23.2	18-27	1.6–2.6	13.0-14.3	3.6–16.9
	Avg±SD	10.1±0.6	5.6±1.5	20.1±7.0	22±12	2.1±0.7	13.8±1.9	9.1±7.0
M8	Min-Max	9.1-10.5	3.6-7.0	20.5-23.4	22-26	1.8–3.8	13.2-15.6	4.0–10.5
	Avg±SD	9.8±1.7	5.3±2.4	22.1±3.7	24±6	2.8±1.4	14.2±3.1	7.0±3.2
M9	Min-Max	8.2-10.2	3.4–6.5	15.3±23	16-23	1.3-1.9	11.4–11.5	4.0–7.7
	Avg±SD	9.2±1.4	5.0±2.2	19.4±4.1	19±5	1.6±0.4	11.5±0.7	5.9±2.6

Characteristic of heavy metals in sediment is depend on many factors, however, this study just considered pH and %LOI factors. Concentration of %LOI in sediment of this area ranges from 2.3 to 16.9 %. The highest of %LOI was determined at M1, M6 and M7, where directly receiving the discharge from upland activities. These results are consistent to the data at Bardawil-Egypt, but much higher than Cabiunas-Brazil.

3.2. Distribution and variation of heavy metals in the sediment

Concentration of As, Pb and Hg investigated for 3 months (March, May and August) from 9 stations was presented in the Table 3. There was a variation of heavy metals concentration in the sediment of Sam Chuon lagoon in spatial and temporal. Concentration of As, Pb and Hg were ranging 1.18-6.24 mg/kg, 4.83-22.13 and 0.0-2.64, respectively. In which, As and Pb tend to increase from March to Augsust, while Hg was found highest in March. The highest concentration of Hg was detected at station M3, where close to the ship construction company. This result might be explained that concentration of Hg in sediment mainly received from upland sources. In comaparison to Vietnamese regulation for sediment quality QCVN43:2012BTNMT, the concentration of investigated metals was below the regulation, excepted concentration of Hg at stations M1, M2, M3 were higher.

In general, there was no significant relationship between heavy metals and selected water quality parameters, except for Pb with DO, EC and salinity in surface water. Pb also have correlation with organic matter in the sediment.

Table 3. The variation of heavy metals in the surface sediment.

Sites	As (mg/kg)			Pb (mg/kg)			Hg (mg/kg)		
	March	May	August	March	May	August	March	May	August
M1	1.55	4.67	6.24	17.64	13.66	22.13	0.43	2.22	0.14
M2	1.58	2.47	3.31	14.79	7.67	13.65	0.37	0.74	0.26
M3	1.67	4.01	2.22	7.44	4.83	8.86	2.64	0.54	0.23
M4	1.18	4.07	2.39	5.55	7.97	6.47	0.62	0.51	0.14
M5	1.45	3.12	5.44	8.18	4.83	15.43	0.41	0.51	0.26
M6	1.45	4.17	3.13	8.60	6.24	7.75	0.35	0.60	0.12
M7	1.64	3.55	5.61	9.33	5.40	13.79	0.59	0.43	0.28
M8	1.67	3.95	4.42	6.90	6.26	15.21	LD	0.31	0.24
M9	(*)	3.10	4.24	(-)	6.53	13.67	(-)	LD	0.08

3.3. The correlation coefficiency of heavy metasl and surface water quality parameters

Table 4 shows the Pearson correlation of selected metals and water quality parameters.

Table 4. Pearson correlation coefficient of As, Hg, Pb and water parameters (n = 26, p < 0.05).

	COD	BOD5	DO	Salinity	EC	TDS	pH	As	Hg	Pb
COD	1									
BOD5	0.0005	1								
DO	-0.29	0.6521	1							
Salinity	0.4377	-0.292	-0.724	1						
EC	0.4533	-0.283	-0.723	0.9991	1					
TDS	-0.124	-0.306	-0.736	0.3112	0.3067	1				
pH	0.2277	-0.124	-0.115	0.2043	0.214	0.147	1			
As	0.2313	-0.08	0.2941	-0.002	-0.007	**-0.716**	-0.023	1		
Hg	-0.156	-0.322	-0.285	0.1929	0.1707	0.3486	-0.186	-0.097	1	
Pb	**-0.461**	0.1627	**0.5822**	**-0.642**	**-0.654**	-0.36	-0.178	0.4248	-0..076	1

3.4. Ecological risk assessement of As, Pb and Hg

In order to assess the ecological risk of As, Pb and Hg at the study area, several indices were calculated, including: contamination factor (CF), enrichment factor (EF), geoaccumulation index (Igeo) and ecological risk index (ERI).

The contamination status of selected heavy metals in the sediment of present study was determined base on CF index, the contamination degree at the sampling sites shows in the Table 5. There was a different contamination of selected heavy metals, the order of contamination factor of investigated metals was Hg>As>Pb. Most of the sampling sites showed that Hg was medium or high contaminated, while As and Pd were low or medium.

In overall, the highest EF of Sam-Chuon area was Hg with 6.79, following was As and Pb. Table 6 shows that the enrichment factor of Hg has a significant higher than As and Pb, the order of EF at sampling sites was M3>M5>M1>M7>M2>M6>M8>M9. The higher EF of Hg was close to the market, ship instruction area or agriculture (M3, M5, M1). This explained that the

contamination of Hg in the sediment of Sam Chuon lagoon was contributed by the discharge from human activities.

Table 5. CF and EF at the study sites.

Site	CF value						EF value					
	As		Hg		Pb		As		Hg		Pb	
	CF	Group	CF	Group	EF	Group	EF	Group	EF	Group	CF	Group
M1	4.15	2	11.65	3	1.51	0	1.51	0	8.05	2	0.82	1
M2	1.29	1	5.72	2	1.26	0	1.26	0	5.57	2	0.78	0
M3	1.39	1	14.17	3	1.64	0	1.64	0	16.79	2	0.56	0
M4	1.34	1	5.31	2	1.68	0	1.68	0	6.67	2	0.56	0
M5	1.76	1	4.89	2	3.21	1	3.21	1	8.94	2	1.16	0
M6	1.54	1	4.43	2	1.65	0	1.65	0	4.76	1	0.54	0
M7	1.90	1	5.38	2	2.12	1	2.12	1	6.01	2	0.71	0
M8	1.76	1	2.29	1	2.67	1	2.67	1	3.48	1	0.96	0
M9	1.93	1	0.53	0	2.97	1	2.97	1	0.81	0	1.04	0

Note: CF≤1: Low pollution; 1≤CF≤3: Medium pollution; 3≤CF≤6: High pollution;

Table 6. Caculation of I_{geo} and ER of selected heavy metals at Sam Chuon lagoon.

Site	As		Hg		Pb		As		Hg		Pb	
	I_{geo}	Lev.	I_{geo}	Lev.	I_{geo}	Lev.	ER	Lev	ER	Lev.	ER	Lev.
M1	1.13	2	3.54	4	0.25	1	21.85	0	465.92	2	5.94	0
M2	0.37	1	2.52	3	-0.32	0	12.91	0	228.96	1	4.01	0
M3	0.47	1	3.82	4	-1.09	0	13.86	0	566.70	2	2.35	0
M4	0.42	1	2.41	3	-1.17	0	13.41	0	212.40	1	2.22	0
M5	0.81	1	2.29	3	-0.66	0	17.56	0	195.52	1	3.16	0
M6	0.62	1	2.15	3	-0.99	0	15.36	0	177.30	1	2.51	0
M7	0.92	1	2.43	3	-0.66	0	18.96	0	215.04	1	3.17	0
M8	0.82	1	1.20	2	-0.67	0	17.61	0	91.70	0	3.15	0
M9	0.95	1	-0.92	0	-0.57	0	19.31	0	21.15	0	3.37	0

*Note: * I_{geo} level: $I_{geo} \leq 0$: Unpollution; $1 < I_{geo} \leq 2$: Low pollution; $2 < I_{geo} \leq 3$: Medium pollution; $3 < I_{geo} \leq 4$: High pollution; $4 < I_{geo} \leq 5$: Very high pollution- *ER <150: Low risk; 150 < ER ≤ 300: Medium; 300 < ER ≤ 600: High; ER > 600: Extremely.*

The geoaccumulation index was used to evaluate the impact of human activities. The order of I_{geo} at study area was 2.16, 0.72 and -0.65 of Hg, As and Pb, respectively. This result depicted that the study area was strongly contaminated of Hg from anthropogenic sources.

In terms of evaluating the risk levels of selected metals in the lagoon, ecological risk index (ERI) was calculated. The result presented in the Table 7.

Table 7. Pollution load index (PLI) and ecological risk index (ERI) of heavy metals at Sam Chuon lagoon.

Sites	As		Hg		Pb		PLI		ERI	
	ER	Group	ER	Group	ER	Group	PLI	Level	ERI	Level
M1	21.85	0	465.92	2	5.94	0	3.11	1	493.71	4
M2	12.91	0	228.96	1	4.01	0	1.81	1	245.88	3
M3	13.86	0	566.70	2	2.35	0	2.10	1	582.91	4
M4	13.41	0	212.40	1	2.22	0	1.47	1	228.03	3
M5	17.56	0	195.52	1	3.16	0	1.76	1	216.24	3
M6	15,36	0	177,30	1	2,51	0	1,51	1	195,16	2
M7	18,96	0	215,04	1	3,17	0	1,86	1	237,16	3
M8	17,61	0	91,70	0	3,15	0	1,37	1	112,47	1
M9	19,31	0	21,15	0	3,37	0	0,88	0	43,83	0
Average	16,76	0	241,63	1	3,32	0	1,76	1	261,71	3

Note: ERI < 100: Low risk; 100 < ERI < 150: Medium risk; 150 ≤ ERI < 200: High risk; 200 < ERI < 300: Very high; ERI > 300: Extremely high risk.

The data presented that the ecological risk of As, Hg and Pb at Sam Chuon lagoon were from low to medium, the order of ER for single elements was Hg>As>Pb. There was an important significant difference between elements or stations. The range of ER for As and Pb was range from 12.91 to 21.85 and 2.22 to 5.94, respectively. In terms of study sites, the ER group might divided as follows: low risk: M8 and M9; medium risk: M2, M4, M5, M6 and M7; high risk: M1 and M3. This result also coincided with the study conducted in Lagos lagoon, the high risk of heavy metals is closely relative with the anthropogenic activities [2].

To calculate the overall toxicity of the study area, the pollution load index (PLI) and ecological risk index (ERI) were used to assess the intergrated pollution levels of As, Hg and Pb. Results of PLI show that pollution level of study area was polluted of As, Hg and Pb with the average value of 1.76. Among sampling sites, the higher pollution was detected at M1 (3.11), M3 (2.10) and M7 (1.86). Meanwhile, ERI value has a wide range from 43.88 to 582.91. The extremely high risk was occured at M1 and M3, the lowest risk found at M9 where closed to the Thuan An estuary. ERI determined in Sam Chuon lagoon was higher than the similar lagoons in the world [1, 2].

4. CONCLUSIONS

Contamination of heavy metals in the sediment is an important problem for the lagoons. Basing on the investigation results from Sam Chuon lagoon, concentration of heavy metals was met the criteria standard of Viet Nam for the sediment, except for Hg at some stations. However, calculation of risk indices showed that Sam Chuon lagoon are polluted by Hg, As and Pb. The higher of ecological risk was occurred at the stations close to the anthropogenic activities, and Hg presented the highest ecological risk in the study area.

Acknowledgment. The study was supported by Hue University under the project Code DHH 2016-01-91. The authors also thank to QUATEST-II in Danang for a partly support for the analysis.

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