ENVIRONMENTAL MONITORING STUDY USING BIVALVES AS BIOINDICATOR FOR POLLUTION CONTROL AND SUSTAINABLE DEVELOPMENT IN THE CENTRAL COASTAL REGION OF VIETNAM

1. INTRODUCTION

There have been studies on the use of organism species as bioindicators for environmental quality monitoring and pollution control. Depending on the physic- chemical properties and environmental of pollutants as well as biological characteristics, accumulate ability of the organism can be select as environmental bio- indicators accordingly.

Pollutants affecting marine ecosystems include a wide range of synthetic organic chemicals, (Substances of particular concern are PCBs, pesticides, dioxin and some industrial solvents); diverse heavy metals and alloys, but also, alternatively, toxins and pathogenic species; pharmaceuticals.v.v. All these pollutants reach the ocean floor through coastal region, which connects pollutions to the marine ecosystem. Though coastal region are highly productive, dynamic and much diversified regions, the entry of these chemicals in the biotic system is much easier. From the marine biotic communities the bottom dwelling mollusks have a tremendous capacity of bioaccumulation. Since the coasts are more prone to the accumulation of all toxic chemicals and there is a higher chance of accumulation in the body of mollusks.

Bivalves species are good bioindicators considering their ability to filter large volumes of sea water and thus highly to accumulate trace contaminants. Bivalves have been particularly used as bioindicators in many countries for marine pollution monitoring. These species are mollusks, lives at bottom depths, directly strongly affected by tides and coastal waters. These animals are adaptable or very sensitive to the environment. These species are often highly susceptible to physiological and biochemical conditions.

Over the last three decades, Vietnam has undergone rapid economic development. Recently, human health concerns related to the occurrence of pollutants such as POPs and heavy metals in aquatic environments in Vietnam have been greatly increasing. In recent years, there are industry and tourism that has strongly developed in the Central region Vietnam. In coastal marine areas of the Central region Vietnam is still receiving the large discharges sources containing pollutants from the mainland to the sea. To manage contaminated coastal sites and prevent adverse effects on human health, the Vietnamese government has undertaken a number of monitoring program. However, very few extensive monitoring studies carried out in the coastal areas of the Central Vietnam.

2. AIMS

- Determination concentration PCBs and heavy metals in sediment and bivalves organisms in coastal areas in Quy Nhon, Binh Dinh province
- Determination the bioaccumulation of POPs/PCBs and heavy metal for each bivalves organisms
- Assessment the current contamination status by heavy metals and PCBs/POPs in Quy Nhon, central coastal region of Vietnam
- Based on the findings of this study can be proposed the monitoring measurement using bivalve's species in order to pollution control and coastal marine environmental management of Vietnam.

3. PROCEDURES

3.1. SAMPLING

-**Location**: The coast long of Quy Nhon is 72 km. Quy Nhon citis located 13.78 latitude and 109.22 longitude and it is situated at elevation 7 meters above sea level. (Figure 1).

-**Collection**: Sediment samples and 3 bivalves species samples were collected in August and September 2019 from tens location in coastal areas Quy Nhon belong to Binh Dinh province, central Vietnam (Figure.1).

+ **Sediment collection**: The sediment samples of the top 20cm surface centimeter were collected with a polyethylene spool or Ekman grab, then placed in a plastic bag, which were stored in an ice box at 4^0C, to be transported to the laboratory. There sediment samples were dried at room temperature, and then were sieved through a nylon mesh to obtain particles smaller than 0.2mm in diameter for determination of heavy metal concentration. For each sediment sample, 3-5Ige gram was taken for heavy metal and POPs/PCBs analysis.

+ **Bivalves collection**: About 10-15 numbers of the same sizes of each bivalve species (*Crassostrea rivularis, Chlamys nobilis,* and *Anadara grasnosa*) were picked by hand from then locations and then put in ice box at 4^0C to be transported to the laboratory. The tissues were separated by a plastic knife and dried at 110^oC during two days to constant dry weight. These dried tissues were then stored in a polyethylene bag to be kept laboratory condition for the determination of heavy metals and PCBs concentrations.

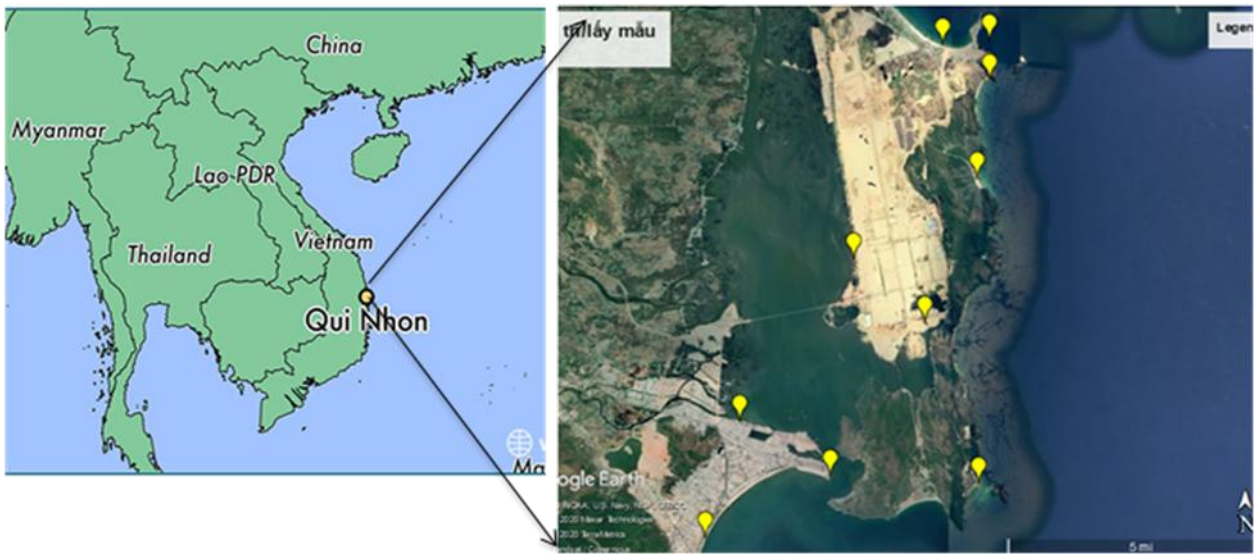

Figure 1. Map of sampling location in Quy Nhon coastal area belong to Binh Dinh province, central of Vietnam

Table 1: Characteristic description of sampling location in Quy Nhon coastal area

	Site mark	Location	Coordinates (Longitude-latitude)	Characteristics description
1	VT1	Quy Nhon Beach	13°45'06.7"N 109°12'60.0"E	Beach area
2	VT2	Port of Hai Doan 48	13°46'07.9"N	It is a big harbor with

			109°15'05.2"E	many boats and ships for trade
3	VT3	Hà Thanh River mouth	13°47'02.3"N 109°13'34.7"E	It is the location of concentrated aquaculture activities
4	VT4	Nhon Hoi Bridge	13°48'40.0"N 109°16'39.7"E	There are civil transport activities
5	VT5	Thị Nại lagoon (outside of lagoon)	13°46'00.3"N 109°17'33.3"E	The location of concentrated aquaculture activities
6	VT6	Nhơn Hội area	13°53'15.0"N 109°16'58.0"E	Location near the area is building factories located in Nhon Hoi economic zone
7	VT7	Nhon Ly coastal area	13°52'39.4"N 109°17'44.8"E	Human activities: people living, trading…
8	VT8	Nhơn Lý port bridge	13°53'19.0"N 109°17'44.8"E	Port area, many boats, ships anchored
9	VT9	Ky co coastal area	13°51'02.6"N 109°17'32.4"E	Beach area
10	VT10	Thị Nại lagoon (inside of lagoon)	13°49'42.5"N 109°15'28.7"E	Location is under the middle of Thi Nai bridge

3.2.ANALYTICAL METHODS

3.2.1. For Heavy metals: Concentration of Hg, Pb, Cd, Cu, Cr, were analyzed in 10 sediments and 30 bivalves samples using ICP-MS. The methods used for sample preparation, digestion, and quantificational analysis were established, generating satisfactory analytical precisions which represented by relative standard deviations (RSD) ranging and recoveries showing in Table 2.

Table 2. Estimation of the repeatability of the heavy metals analysis by the Relative standard deviations (%) and recovery (%)

RSD (%)					
	Hg	Pb	Cd	Cu	Zn
Sediment	0,27	0,900	0,070	1,63	0.85
Bivalve organism	0,42	0,16	0,0102	1,08	0,50
Recovery (%)					
Sediment	95-101	92-105	93-105	99-109	88-102
Bivalve organism	89-102	91-110	95-110	97-109	90-105

3.2.2. For PCBs and organochlorin pesticides

PCBs in the dried samples were analyzed using GC-MS, after extraction with hexane/acetone (1:1 v/v) and clean-up with gel-permeation chromatography and activated silica-gel.

3.3.Data analysis

a) Concentration of heavy metals in sediment

$C_s = \frac{C_{do} \times V_{dm}}{m} \times K$ (mg/kg dry sediment)

In which: Cs: heavy metals contents (mg/kg dry sediment).

C_{do}: heavy metals concentraion measured (mg/L).

V_{dm}: sample volume; m: sample weight (g); K: dry coefficient of sediment

b) Concentration of heavy metals in bivalves species

$$C_t = \frac{C_{do} \times V_{dm}}{m} \text{ (mg/kg dry organism)}$$

In which: C_t: content of heavy metals (mg/kg) in bivalve species.

C_{do}: metal concentration measured (mg/l).

V_{dm}: volume of solution measured on (ml). m: sample weight (g)

c) **BSAF** (Biota-sediment Accumulation Factor)

$$BSAF = \frac{C_t / f_L}{C_s / f_{OC}}$$

In which: C_s: content of heavy metals (mg/kg) in sediment

-Ct is the concentration of heavy metal in the tissue of bivalves species (µg / g of dried meat tissue).

- fL: lipid content in the tissue of living organisms (%).
- foc: content of organic carbon in sediments (%)

d) **Igeo** (Geological accumulation Index)

Igeo=Log2 Cx/1,5 Bx

In which: C_x: content of heavy metals (mg/kg) in sediment

Bx : background concentration value of metal x in the Earth's crust

(Bx value according to Turekian K. K., and Wedepohl K. H. (1961):

4. RESULTS AND DISCUSSION

4.1. Concentration of heavy metals in sediment

Concentration of Hg, Pb, Cd, Cu, Zn were found in almost sediment samples and collecting location. The concentrations of heavy metals were showed a variation between the metals and between sites. Metal concentrations in the sediments ranked in the following order: zinc > copper > lead > cadmium> mercury. Elevated concentrations of heavy metals were showed high levels from 5 locations, such as VT1, VT2, VT3, VT4 and VT5, as show in Table 3 and Fig. 2. With the described characteristics of each sampling location (Table 1), the VT1 location is the stationed area of naval army units 48, VT 2 and VT4 are the big ports, VT3 and VT5 farming and aquaculture areas. . The area is rich in the cultivation, manufacturing, transportation and tourism activities of Quy Nhon City....

Table 3: Concentration of Hg, Pb, Cd, Cu, Zn in sediment (mg/kg dry weight)

Site mark	Hg	Pb	Cd	Cu	Zn
VT1	0.072	4.109	3.23	20.91	41.62
VT2	**0.083**	**6.225**	**2.34**	**41.62**	**165.04**
VT3	**0.039**	**3.694**	**4.15**	**163.04**	**58.37**
VT4	0.016	0.756	1.66	58.37	51.20
VT5	N.D.	4.651	1.78	51.20	39.77
VT6	0.040	2.321	1.54	39.71	51.42
VT7	0.014	0.754	2.03	51.42	57.91
VT8	0.012	1.173	2.35	57.91	23.99
VT9	0.029	2.023	1.28	23.99	36.35
VT10	0.032	3.028	1.97	28.65	41.62

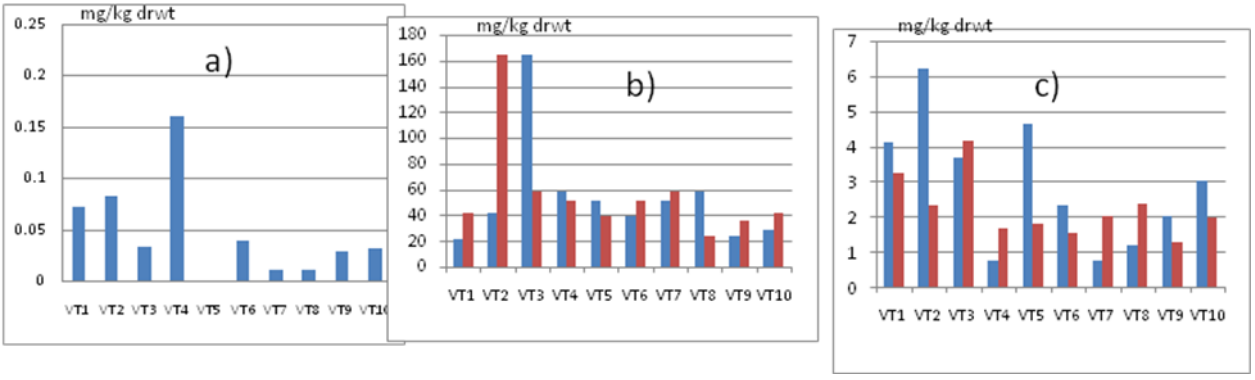

Fig.2. Concentration of heavy metals in sediment collected at Quy Nhon coastal area (a) Hg, b) Cu and Zn, c) Pb and Cd

Table 4. Assessment of environment status of heavy metal based on Sediment Quality Guideline (mg/kg dr.wt)

Quy Nhon coastal area (n=10)	Hg	Pb	Cu	Cd	Zn
Minimum	0.012	0.754	**20.91**	1.28	23.35
Maximum	**0.083**	6.225	**163.04**	**4.15**	**165.04**
Threshold effect level (TEL)[a]	0.70	112	108	42	271
Probable Effect Level (PEL)b	0.70	250	110	10	110
Threshold effect level (TEL)[b]	0.15	112	108	4,2	160
Effect range – low (ERL)[b]	0.13	31	16	0,6	26

Note: [a] QCVN 43/2012/BTNMT National Regulation for Sediment Quality of Vietnam

[b]Sediment Quality Guideline of Canada

In order to assess the current environmental heavy metal pollution in sediments, the method of SQGs (Sediment Quality Guideline and I_{geo} values were used. The result of the content of some heavy metals in sediments in Quy Nhon coastal area is compared with the National Technical Regulation on Sediment Quality – QCVN 43: 2012/BTNMT and Guideline on Sediment Quality of Ontario, Canada (1993) - the prescribed values to protect aquatic systems to assess the level of pollution and accumulation of heavy metals in the study area (Table 4)

The results of Hg content in sediment samples ranged from 0.012 mg/kg (at VT8 location) to 0.083 mg/kg dry wt (at VT4 location). Concentration of Hg in all samples did not exceed the limit value of sediments (0.7 mg/kg dr wt) is regulated in QCVN 43: 2012/BTNMT sediment quality standards.

The results of Pb content in sediment samples ranged from 0.754mg/ kg (at VT8) to 6.225 mg/kg dry weight (at VT2 location). The content of Pb in all samples are within the limits of QCVN 43:2012/BTNMT National Technical Sediment Quality Standards as well as in Ontario - Canada sedimentary quality guideline.

The metal content results in Table 2 also show that Cu content in sediment samples ranges from 20.91 to 163.04 mg/ kg dry weight. The content Cu of almost location were found within the limits of QCVN 43:2012/BTNMT, exception of VT3 location (163.04 mg/kg dr wt) However, according to the Ontario - Canada sediment quality guidelines, Cu concentration in sediment of all location were higher the Effect low Level (LEL).(16mg/kg dr wt).

With the content range from 23.99 to 165.04 mg/kg dry weight, concentration of Zn in sediment samples at all location do not exceed the limit value specified in QCVN 43: 2012 / BTNMT. However, according to the Ontario - Canada sediment quality guidelines, Cu concentration in sediment of all location were higher the Effect low Level (LEL).(23 mg/kg dr wt).

Zinc has a similar trend to copper with location differences: the highest concentrations in the surface sediment occur in the VT2 and VT3 as Cu:163,04 mg/kg dr wt and Zn:165,04 mg/kg dr.wt, respectively. These location are closed the big harbour and concentrated aquaculture. The sampling period in August and September is the time when the most exciting activities of the year in Quy Nhon area. In this study, the sampling period in August and September is the time when the most exciting activities of the year in Quy Nhon area. Because the weather is good at the moment, no rain, no floods or storms, so crowded tourists, ports with busy boats and aquaculture areas are also very developed. High concentration of Zn and Cu can showed high sign of anthropogenic contamination sources. Sometime Zn and Cu in sediment are from natural source as their natural presence in the lithosphere.

4.2. Concentration of heavy metals in sediment (not finished yet and to be continued)

Table 5. Concentration of Hg, Pb, Cd, in 3 bivalve species (mg/kg dry weight)

	Crassostrea rivularis			*Chlamys nobilis*			*Anadara granosa*		
	Hg	Pb	Cd	Hg	Pb	Cd	Hg	Pb	Cd
VT1	0.098	2.941	1,26	0.205	1.499		0.028	11.382	
VT2	N.D	3.323	1,68	0.469	4.463		0.025	5.134	
VT3	0.018	3.575	1,45	0.029	0.249		0.039	8.954	
VT4	0.108	3.126	1,48	0.124	4.870		0.015	5.164	
VT5	N.D	3.541	1,28	0.059	3.615		0.080	3.559	
VT6	0.002	3.462	0,16	N.D	1.474		0.019	7.711	

VT7	0.012	1.270	2,34	0.029	1.137		0.006	4.683	
VT8	0.032	3.426	1,45	0.024	1.258		0.038	6.362	
VT9	0.024	3.157	1,03	0.035	1.984		0.085	4.194	
VT10	0.038	3.146	1,97	0.127	2.035		0.073	8.654	

Table 6. Concentration of Cu, Zn in 3 bivalve species (mg/kg dry weight)

TT	**Site**	***Crassostrea rivularis***		***Chlamys nobilis)***		***Anadara granosa***	
		Cu	Zn	Cu	Zn	Cu	Zn
1	VT1	66.71	602.61	4.64	86.008	1.32	110.088
2	VT2	65.80	568.58	15.16	77.443	64.80	69.347
3	VT3	75.24	573.97	18.17	56.912	61.68	89.378
4	VT4	60.03	685.63	19.67	58.254	89.31	111.955
5	VT5	59.73	804.50	17.92	55.900	80.54	80.367
6	VT6	76.82	757.42	15.87	94.049	-	83.663
7	VT7	49.53	486.20	13.84	69.945	75.10	115.570
8	VT8	59.73	581.19	19.49	73.065	-	102.009
9	VT9	55.08	548.70	20.91	63.854	-	83.4
10	VT10	48.37	593.00	18.02	53.3	117.51	101.5

4.3. Concentration of PCBs in bivalve species (7 samples)

Table 6. Concentration of PCBs (ng/g wet weigh)

	Sample1	Sample2	Sample3	Sample4	Sample5	Sample6	Sample7
Total PCBs (61 PCB congeners)	7.63	8.18	9.59	8.69	0.05	0.03	0.02
Total indicator PCBs (6 PCB congeners)	2.94	3.19	3.77	3.34	0.05	0.03	0.02
Total dioxin like-PCBs (12 PCB congeners)	0.28	0.27	0.38	0.32	0.00	0.00	0.00
Total TEQ	0.008	0.008	0.011	0.010	0.000	0.000	0.000

dioxin like-PCBs (12 PCB congeners							

Table 7. Concentration of PCBs (ng/g lipid wet weigh)

	Sample1	Sample2	Sample3	Sample4	Sample5	Sample6	Sample7
Total PCBs (61 PCB congeners)	91.69	84.70	77.36	211.54	1.36	0.81	0.71
Total indicator PCBs (6 PCB congeners)	35.29	33.00	30.46	81.34	1.36	0.81	0.71
Total dioxin like-PCBs (12 PCB congeners)	3.33	2.83	3.03	7.79	0.000	0.000	0.000
Total TEQ dioxin like-PCBs (12 PCB congeners	0.00010	0.00008	0.00009	0.00023	0.00000	0.00000	0.00000

5. RECENT PUBLICATION

1. Le Thu Thuy, Le Thi Hai Le, Nguyen thi Thuc Anh, Luong Ngan Ha, Nguyen Thanh Thao (2018). Concentration of some heavy metals (Cd, Pb, Zn) in bivalve species in Quy Nhon coastal area, Binh Dinh province. *Journal of Analytical Science (ISSN-0868-3234), T-23, Vol 4A, 214-2019*
2. Le Thi Hai Le, Tran Hong Con, Le Thu Thuy (2018). The retention and transformation of some heavy metals in urban dredged sludge. *Journal of Analytical Science (ISSN-0868-3234), T-23, Vol 4A, 169-176*
3. Le Xuan Sinh, Le Thi Hai Le, Mai Huong (2019) Bioaccumulation of mercury in clams (*meretrix lyrata*) cultured at Bach Dang estuary: A recommendation for safely daily dosage consumption of Clam in Vietnam (2019). *The 20th International Conference on Pollutant Responses in Marine Organisms (PRIMO 20) in May 19-22, 2019, Charleston, South Caroline, USA. P59*
4. Le Thi Hai Le, Le Thu Thuy, Do Le Chinh (2019). Concentration of Hg, Pb and Cd in ovsters (*Crassostrea rivularis)* and surface sediments in coastal areas of Binh Dinh province. *Journal of Analytical Science (ISSN-0868-3234), T-24, Vol 4A, 132-138*