QUANTITATIVE RESESRCH FOR POLLUTION LEVELS IN MARINE SEDIMENTS OF HALONG BAY BY NUCLEAR TECHNIQUE

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ABSTRACT: Under the theme of "Quantitative study of pollution levels in marine sediments of Halong bay by nuclear techniques" conducted from June 2011 to June 2013, the authors conducted monitoring, sediment samples collected in the bay below the sediment column at 8 locations, in which 7 columns located at the estuary near Tuan Chau Island and 1 column at the area near the harbor of Cam Pha. The column samples were taken to the laboratory, cut slices with a distance of 2 cm in the form of frozen and conduct tests of radioactive Pb-210 to determine the rate of sediment in the survey area. Evaluation results based on the method by determining ^{210}Pb, the sediment rate showed speed in the survey area ranged from 0.3 cm.a^{-1} to 1.2 cm.a^{-1} and an average of 1.0 cm.a$^{-1.}$ The slices of sediment samples (110 samples) were analyzed heavy metals (KLN) and As elemental by ICP-MS method. These sediment sample also were analyzed for simultaneous determination of N and P and total organic carbon (TOC). Results showed that heavy metal concentrations and As is smaller than the value specified in the National Technical Regulation on Sediment Quality of Vietnam (QCVN), phosphorus concentration less than that can cause harmful effects, but the concentration of total nitrogen and organic carbon that may exceed be harmful as directed by Canadian standards (Persuad et al. 1992). The concentration data in the Halong bay sediment were processed by statistical software SPSS-18, results showed high correlation between the quality TOC, N, P, K and correlation the majority of KLN, this proves the origin of sediments is part of the natural soil components and parts (TOC, N, P, K) is due to the activity of human activity as well as by agricultural fertilizers. The average content of elements in sediments Halong be compared with other data published works of sediment Quang Ninh area, the results show the correlation figures are also high. However, the results of the analysis of KLN and As in Halong sediment of this work are smaller than those previously published by the total digestion method. The reason in this work may be from the treatment of sediment sample by incomplete digestion method using acetic acid.

Keyword: *marine sediment, heavy metal, sedimentation rate.*

I. INTRODUCTION

Coastal areas region are under pressure by the process of economic and social development. Problem of marine environmental protection, preservation and conservation of coastal ecosystems are particularly concerned to maintain the stability and long-term economic development, as well as ensure sustainability of community health. The study and evaluation of pollution of the marine environment through the determination of heavy metals (KLN) or other toxic substances such as As in the environment and the bottom sediment seawater is particularly interested. The increase in heavy metal accumulation in some marine sediments are considered to be derived from the continued growth of the industry, the mining operation and that causes red tide phenomenon. Red tide causing marine ecosystem destruction and death if consumed seafood in the incidents.

Nuclear Engineering and isotope techniques have been widely used to study the marine environment, in particular the implementation of the developed countries have laboratories with modern equipment and staff have more experience. The analysis of nuclear techniques and related applications in research and critical alerts are mainly marine environment include: a) Warning

marine pollution by toxic heavy metals As, Cd, Co, Cr, Cu, Pb, Hg, Ni, Zn, Se. b) Warning pollution of the marine environment by radioactive elements U, Th, ^{210}Po, ^{210}Pb, ^{226}Ra, ^{90}Sr, ^{137}Cs, $^{239.240}$Pu and c) Look at the environmental process for the ^{14}C, ^{210}Pb, ^{230}Th isotope indicators to get an understanding and assessment processes and pollution source pollution (due to natural or human impacts). One of the aproach often used in the study is sampling marine sediment column, content of analysed KLN and amount of ^{210}Pb isotope sediment slices in are determination. Based on the amount of radioactive isotopes of lead scientists will be able to determine sedimentation deposition time with KLN.

The purpose of this study is determination of the age of sediments along the Halong bay with some heavy metal content to learn the history of pollution generated in the ecosystem of the world cultural heritage by UNESCO.

II. MATERIAL AND METHODS

- Characteristics of the study area

The study area is Ha Long bay in Quang Ninh Province, and the areas near of coal mining operations (Nui Beo-Cam Pha), with production activities and export of cement, with aquaculture activities in Bay, tourism activities sightseeing and nature this is also where the population density increased.

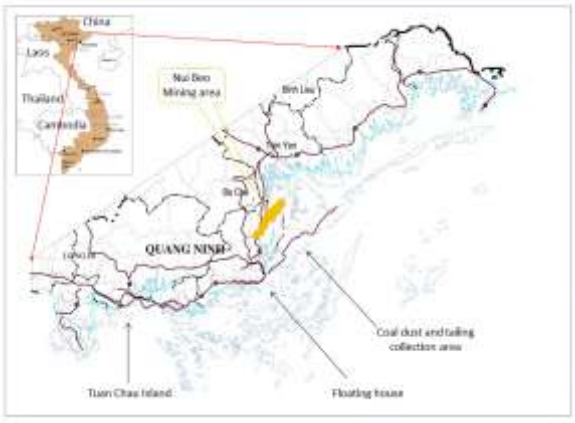


Figure 1: The study area of Ha Long Bay, Quang Ninh.

- Sampling

Sampling location is divided into two areas Binh Huong estuary, near Tuan Chau Island, where there are many beach clam, scallop (Figure 2) and river creek bridge No 20 area near Cam Thinh ward (Figure 3), where the waste products of coal mining Nui Beo be poured into the sea . Sampling place also is close to the cement factory at Cam Pha port.

Figure 2: control Sampling positions are triangle mark (HL. ..) and sedimentary columns are circle mark in Binh Huong estuary (1,2,3,4,5), each 1 meter deep sediment columns and sedimentary columns far deviation to the left estuary M2, M1 ...

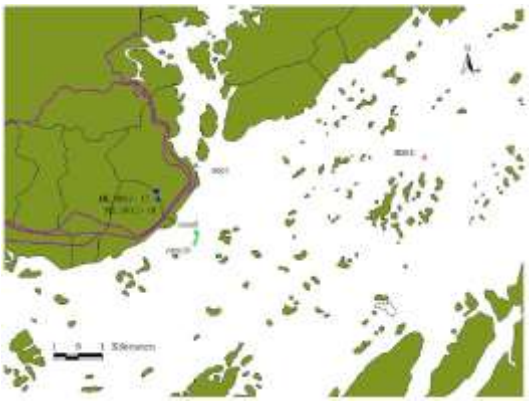


Figure 3: Sampling location near the river creek bridge No 20, Cam Thinh ward, circle
mark are the sediment column samples (6,7,8,9,10) and water samples, controlled soil samples are triangles mark (HL.. .)

- **Methods of analysis**

Methods of analysis components contaminated by sedimentary stratigraphic sections are common methods to assess historical pollution of the marine environment caused by the activities of social nature and the land. To accomplish this task, it is necessary to take steps to: a) Get column marine sediments vertically. b) Cut slices of the sediment column as specified aperture (Usually from 2 to 5 cm). c)Use nuclear methods such as ^{137}Cs, ^{210}Pb to evaluate the rate of sediment or otherwise determine the age of each slice. d)Analysis of the pollution component slices.

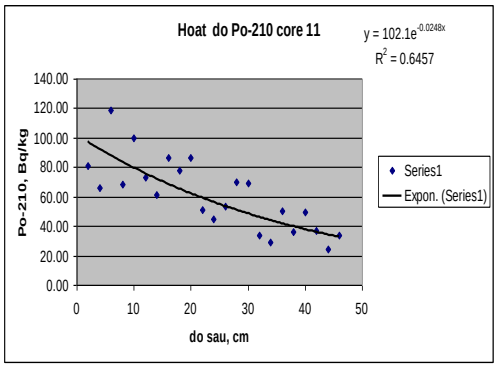
Results pollution assessment in sediments along the transect of the environmental parameters at sea survey is a good basis for evaluating historical pollution of the marine environment due to the operation of natural and social activities caused by humans.

The KLN analysis by ICP-MS method was carried out at Rare Radiation Technology Institute, digestion methods are destructive method using acetic acid is not entirely aimed at the heavy metal pollution assessment. The nuclear techniqes for determination of ^{210}Pb, ^{210}Po was carried out in Institute of Science and Nuclear Engineering, total nitrogen and phosphorus was in the 27 lab Lab of Ministry of Agriculture and Rural Development.

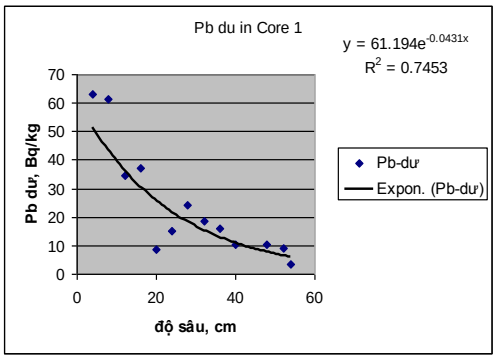
III. RESULTS AND DISCUSSION

- **Sediments rate**

Sedimentation rate was assessed through analysis of radioactive ^{210}Pb and it' daughter ^{210}Po in the sediment slices. ^{210}Pb was analyzed by the gama spectrometer at 47 keV with the HPGe GMX-40 detector in low background lead house. ^{210}Po was analyzed by alpha spectroscopy after sample chemical processing and electrolysis on silver platter. Illustrative example is shown in Figure 4, which can be seen in the sediment rate R at Core 1and Core 11 are 0.76 cm a^{-1} and 1.25 cm a^{-1}, respectively.



R=**1.25cm a^{-1}**



R=**0,76 cm a^{-1}**

Figure 4: Illustration sedimentation rate using ^{210}Pb in the core 1 and ^{210}Po in the core 11.

The combine results of sedimentation rate in Halong bay by two methods are presented in Table 1 below:

Table 1: Comparison sedimentation rate R measured by ^{210}Pb and ^{210}Po methode.

Cores	R (cm.a^{-1}) by ^{210}Pb	R (cm.a^{-1}) by ^{210}Po
Core 1	0.76	
M1	0.75	0.72
M2	0.58	1.01
M3	1.12	1.02
M4		1.16
Core 11		1.25
Core 13		0.31
Core 8		0.27

Over table 1, it can draw the following comments:

- The comparison of sediment assessment rate from 2 methods are generally comparable (shown in column form M1, M3, however, the difference just only in sample M2 column. We have found that the method ^{210}Pb using gamma spectrometer with the reliability is not so high due to gamma energy of ^{210}Pb has a gamma line of 47 keV, which calded "soft gamma line". The measurement of ^{210}Pb in such energy has some difficulties because of the absorbtion effect from material and also the background at this energy is quite high. Meanwhile evaluation method based on the classic ^{210}Po is highly reliable because it uses the internal standard (^{209}Po), and this method is quite sensitive, just small sample (0.5 g) is needed and alpha background spectrum is extremely low.

- Evaluation results of sedimentation rate above are relatively logic. The estuary near Tuan Chau Island have high sedimentation rate (about 1 cm.a^{-1}), which is consistent with preliminary observations the water is muddy, so a lot of sediment forming a shallow beach area where locals take advantage of the terrain to create clam area except for Core 13,which is the river sediment. In contrast, in the area near the town of Cam Pha region (Core 8) the sea sedimentation rate is low (0.27 cm.a^{-1}) look like the prossess of sea sediment.

- **Assess heavy metal pollution and As**

Obtained contents of KLN and As in slices sediments at Halong bay by ICP-MS analysis after incomplete digestion with acetic acid is shown by depth (x-axis) and heavy metal concentrations (y-axis), example illustrated the content of KLN and As at the column M1 as shown in Figure 5. The obtained concentration of KLN and As of sediment in the bay sediment core follow the depth of column M1 is illustrated in Figure 5 shows no systematically chance in the levels of the depth (as well as the age) of the sediment column.

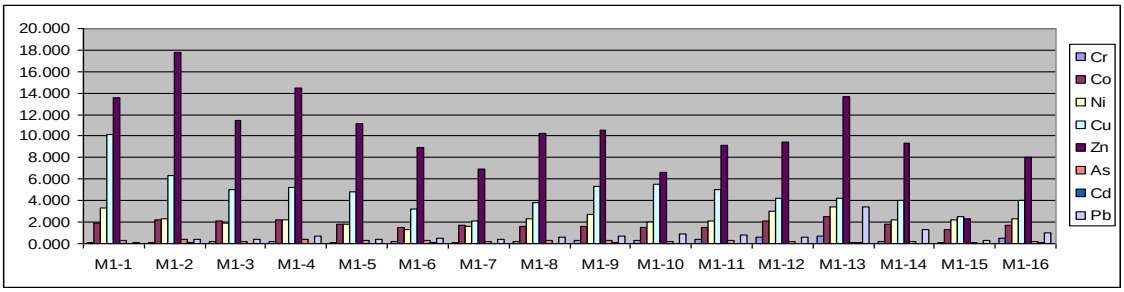


Figure 5: The distribution of heavy metal and As concentrations (mg/kg) in core slices of M1 vs the depth.

The average content KLN and As (mg / kg) of 110 sediment samples from Ha Long bay was shown in Table 2 below:

Table 2: The average content of heavy metal (KLN) and As Halong Bay sediments.

Cores	Cr	Co	Ni	Cu	Zn	As	Cd	Pb
C13	0.29	1.83	2.37	3.01	12.55	0.17	0.06	0.59
C4	0.32	3.88	2.92	3.92	19.40	0.24	0.09	1.72
C1	1.29	4.00	4.83	3.16	33.38	0.13	0.89	1.57
M2	0.24	1.94	2.21	4.96	10.39	0.30	0.01	1.33
M1	4.72	0.78	10.24	0.04	2.30	1.83	0.27	0.25
M3	0.29	1.72	2.35	3.58	6.68	0.19	0.01	0.53
M4	0.44	2.06	2.19	3.19	7.71	0.17	0.02	0.68
C8	0.33	2.59	5.20	3.52	16.24	0.16	0.08	1.18
Average	0.99	2.35	4.04	3.17	13.58	0.40	0.18	0.98
Max	4.72	4.00	10.24	4.96	33.38	1.83	0.89	1.72
Min	0.29	1.83	2.37	3.01	12.55	0.16	0.06	0.59

- **Evaluation N content, TOC, P, K, Fe, Mn in Ha Long bay sediments**

The concentration of N, TOC, P, K, Fe, Mn (%) in sediment at column M1 follow the depth is illustrated in Figure 6 shows no significant difference in the levels vs the depth (as well as the age) of the sediment column.

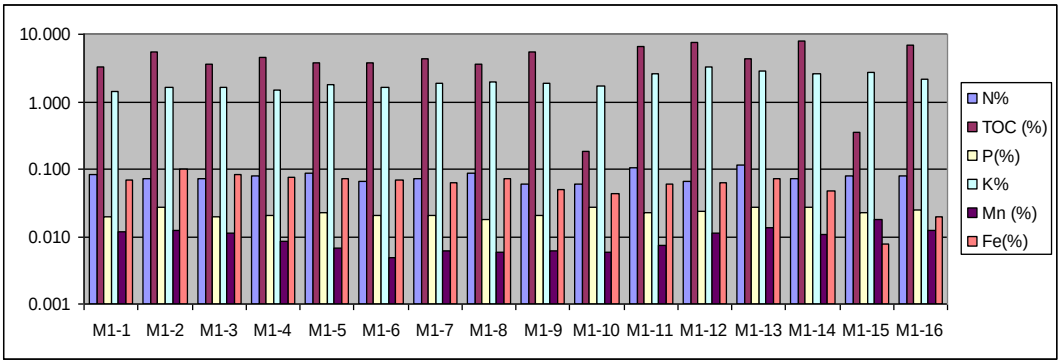


Figure 6: The distribution of N, TOC, P, K, Fe, Mn (%) in core slices of M1 vs the depth.

- **The correlation**

The relationship between the three components of natural radioactivity from U, Th and ^{40}K were compared between control samples (20 samples of surface soil on the banks of the position corresponding to sampling sediment column). Survey results correlations between the three components of radiation above the 20 control samples shown in table 3 and slices of sediment samples (110 samples) shown in table 4

Table 3: The correlation U, Th and K-40 in the control soil.

	U (Bq/kg)	Th (Bq/kg)	K-40 (Bq/kg)
U (Bq/kg)	1		
Th (Bq/kg)	**0.975847**	1	
K-40 (Bq/kg)	0.477029	**0.560903**	1

Table 4: The correlation U, Th v μ K in sediments (110 samples).

	U (Bq/kg)	**Th (Bq/kg)**	**K-40 (Bq/kg)**
U (Bq/kg)	1		
Th (Bq/kg)	**0.804331**	1	
K-40 (Bq/kg)	**0.794712**	**0.918485**	1

Through table 3 on the correlation between the radioactive chain U, TH and ^{40}K in the control sample and table 4 on the relationship between the sequence of radioactive U, Th and ^{40}K in the sediments in the Gulf Ha Long, we can see that in the control sample correlation between U and Th are very tight, but not correlated closely with ^{40}K. This is logical because U and Th chain is closely related to the origin of granite bedrock and relatively independent of ^{40}K. By contrast in the marine sediments bay we found love affair closely and both U, Th and ^{40}K. We know that the ^{40}K level radioactive closely related to potassium ratio stable. Relationship closely in all three series isotopes indicate the presence of additional sources of potassium fertilizer on sediment composition. Here may be due to the impact of human activities due to agricultural production (fertilizer N, P, K).

Table 5: Correlations TOC, N, P, Mn, Fe in sediments (110 samples).

	N%	**TOC (%)**	**P (%)**	**K%**	**Mn (%)**	**Fe (%)**
N%	1					
TOC (%)	**0.623686**	1				
P (%)	**0.756656**	**0.644948**	1			
K%	**0.693325**	**0.654450**	**0.76411**	1		
Mn (%)	**0.538622**	**0.556859**	**0.59097**	**0.664023**	1	
Fe (%)	0.274857	0.312592	0.15927	0.046797	0.252757	1

Table 6: correlation KLN and As in sediments (110 samples)

	Cr	**Co**	**Ni**	**Cu**	**Zn**	**As**	**Cd**	**Pb**
Cr	1							
Co	**0.60330**	1						
Ni	0.46308	0.50956	1					
Cu	-0.23115	-0.06619	0.00301	1				
Zn	**0.73033**	**0.71246**	0.46795	-0.06489	1			
As	-0.37325	-0.1464	-0.26535	0.41225	-0.21581	1		
Cd	**0.86901**	**0.61914**	0.49687	-0.20377	**0.79222**	-0.32374	1	
Pb	0.35524	0.50624	0.25352	0.06431	0.44721	0.094919	0.426958	1

Table 5 shows the correlation of TOC, N, P, Mn, Fe and table 6 shows the correlation of heavy metal and As in sediments. It can be seen there pretty tight correlation between N, P, and K. This TOC, P, K once again (see the relationship in table 4) to predict sediment pollution is caused by human activities in agriculture (fertilizer N, P, K) and tourism. The correlation of the heavy metal and As shown not clear relationship. Only through the variable relationship between Cr, Co, Zn and Cd (the number in bold in Table 6) have seen. In Figure 5, it can be found that the

concentrations of Zn in Halong sediment highly superior to the other heavy metal, so it can be used to judge the amount of other heavy metal such as Co, Cr and Cd in sediment samples.

IV. CONCLUSION

- **Sedimentation rate at the survey location**

Through the evaluation results by the method of Pb-210, Po-210 sedimentation rate in different locations of Ha Long bay ranged from 0.3 $cm.a^{-1}$ to 1.25 $cm.a^{-1}$ and an average of 1.0 $cm.a^{-1}$. This data is consistent over the previously disclosed in the estuarine lagoons and bays in the surrounding area from 0.2 to 2.9 $cm.a^{-1}$ of previously published [1].

- **Assessment of radioactive contamination in sediments Ha Long**

The sediment slices and control samples were analyzed radioactivity. The results showed that natural radioactivity U, Th and ^{40}K in the sediments at the bay's are in environmental background level. The results also showed that the radioactivity of coal in this area is not higher than the background environment. In summary it can be stated without natural radioactive contaminants in sediment samples Halong.

- **Assessment of sediment contamination in Ha Long**

Table 7: The data of the average, maximum, minimum concentrations of Cr, Co, Ni, Cu, Zn, As, K, Mn, Cd, Pb in Halong sediments with values of QCVN.

	Cr	**Co**	**Ni**	**Cu**	**Zn**	**As**	**K%**	**Mn**	**Cd**	**Pb**
QCVN	**160**				**271**	**41.6**			**4.2**	**112**
Average	0.99	2.35	4.04	3.17	13.58	0.40	1.559	100	0.18	0.98
Max	4.72	4.00	10.24	4.96	33.38	1.83	2.458	240	0.89	1.72
Min	0.29	1.83	2.37	3.01	12.55	0.16	1.114	40	0.06	0.59

Through the information on the Table 7 can confirm concentrations of KLN and As in sediments on the bay is not to exceed QCVN. As reported in the article "Comparison of heavy metals in marine sediments from coast areas in East and Southeast Asian countries During the years 2000-2010"[2], the concentrations of the heavy metal (mg/kg) were in range as following:

Cd: 0.13 to 0.89 [maximum in southeast Asia], Cr: 0.09 to 96.0 [maximum in southeast Asia], Cu: 3.0 to 148 [maximal southeast Asia], Ni: 1.0 to 37.4 [maximum in east Asia], Pb: 1.0 to 111 [maximal southeast Asia], Zn: 4.0 to 595 [maximal southeast Asia]. This suggests that the heavy metal concentrations in the sediments in the Ha Long bay is normal and in low concentrations in the general area of East and Southeast Asian.

- **Assessment of pollution P, N, TOC**

In the National Technical Regulation on Sediment Quality of Vietnam- QCVN, the targets for N, P and TOC not given, but can be based on the defined criteria, assessment and management of contaminated sediments Otario region (Canada) in table 9 (Persuad et al. 1992). [3]

It can be seen that (see, comparing the data of Table 8 and Table 9), the concentrations of P in sediments Halong not cause harmful effects to the environment. Conversely nitrogen in sediment samples exceeded the low level effects but not to strong threshold effects. For TOC, the majority of excess low effect even a few samples (100 samples in total) had to have a strong adverse effect to the environment.

Table 8: The average value of the function N, P, TOC (%) in Ha Long bay sediments.

	N%	**TOC (%)**	**P(%)**
Average	**0.079**	**5.630**	**0.021**

Maximum	**0.145**	**11.571**	**0.052**
Minimum	**0.011**	**0.180**	**0.007**
Standard deviation	**0.030**	**2.259**	**0.007**

Table 9: Sediment quality criteria for metals and nutrients units of mg/kg (dry weight).

	Threshold effect (mg/kg)	**Extreme effect (mg/kg)**
As	6	33
Cd	0.6	10
Cr	26	110
Cu	16	110
Fe(%)	2	4
Pb	31	250
Mn	460	1100
Hg	0.2	2
Ni	16	75
Zn	120	820
TOC(%)	**1**	**10**
TKN	**550**	**4800**
TP	**600**	**2000**

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