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STUDY ACCUMULATION CHARACTERISTICS OF HEAVY METALS AND PERSISTENT ORGANIC POLLUTANTS IN COASTAL SEDIMENTS OF MONG CAI CITY, QUANG NINH PROVINCE

SUMMARY OF DISSERTATION ON ENVIRONMENTAL AND NATURAL RESOURCES MANAGEMENT

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INTRODUCTION

1. Necessity of research

With a coastline stretching over 3.260 km, Vietnam has very favourable conditions for developing marine economies such as transport, tourism services, and aquaculture. After the renovation period, the socio-economy has developed rapidly, especially in coastal areas. However, rapid socio-economic development in recent years has been causing great pressure on the marine environment. Mong Cai City, Quang Ninh is a border area between Vietnam and China, prioritized for economic development in Vietnam. Sediments and other coastal environmental components are affected by the economic development of both Vietnam and China and are affected by transboundary environmental impacts from various sources in the basin and coastal circulations according to the oceanographic system. Therefore, if there is a source of pollution, it will lead to the accumulation of pollutants in sediments and seawater, causing increasing damage to the ecosystems in this area, and reducing biodiversity and environmental quality.

Industrial activities in Mong Cai City are quite active in the border area, including seafood processing, mechanical engineering manufacturing, and garment-textile activities, which have created pollutants. There is a lot of farming in Mong Cai and the rest of China's mainland. Chemical fertilizers and pesticides containing phosphorus and chlorine are used on rice fields and other crops. These chemicals are washed away and enter the system of ditches, water channels, streams, and rivers. They are then dumped into the Ka Long River, where they end up on the coast, where they accumulate for a long time. This includes stable organic substances originating from chlorine. Studies have shown that waste sources affect the environment for residents—tourism, livestock, aquaculture, and industry. Studies on the presence of heavy metals in surface sediments, based on monitoring results over many years, indicate an increasing trend. However, the system currently lacks information on the characteristics of sediments and the accumulation of pollutants, particularly heavy metals and persistent organic substances, in the coastal area of Mong Cai. Could you provide answers to the questions regarding the accumulation of heavy metals and persistent organic substances in the coastal sediments of Mong Cai, Quang Ninh region? What is the origin of these pollutants? In the coming time, how will human activities affect the coastal sediments of Mong Cai, Quang Ninh? The student chose the topic "*Study accumulation* *characteristics of heavy metals and persistent organic pollutants in coastal sediments of Mong Cai City, Quang Ninh Province*" for this thesis.

2. Objectives

- Study the accumulation characteristics of heavy metals (Cu, Pb, Zn, Cr, Co, Ni, Fe, V) and persistent organic pollutants (PAHs, OCPs) in coastal sediments of Mong Cai City, Quang Ninh.
- Determine the origin and assess the environmental risks of heavy metals and persistent organic pollutants to the coastal area of Mong Cai City, Quang Ninh.

3. Research contents

(i) Study the overview of the economic and social conditions of the coastal area of Mong Cai City, Quang Ninh;

(ii) Study the distribution characteristics of grain sizes, radioactivity isotopes, and stable isotopes in coastal sediments of Mong Cai City, Quang Ninh;

(iii) Study the distribution and accumulation characteristics of pollutants (heavy metals, PAHs, OCPs) in surface sediments and in sediment cores;

(iv) Identify the origin and risks of heavy metals, PAHs and OCPs in sediments to the coastal environment of Mong Cai City.

4. Scientific and practical meaning of the thesis

➢ ***Scientific meaning***

- Further clarify the current status of accumulation and the possibility of heavy metal pollution and persistent organic pollution in coastal sediments of Mong Cai City.
- Clarify the relationship between pollutants and sediment composition characteristics. Clarify the source of pollutants.

➢ ***Practical meaning***

The thesis results are the basis for warning about the possibility of transboundary pollution and for planning socio-economic development policies to protect the environment and ecosystems in the coastal areas of Mong Cai City and Quang Ninh. The results of the research can be used as a scientific basis for activities to sustainably use natural resources in the study area.

5. New points of the thesis

- The distribution and accumulation characteristics of heavy metals and persistent organic pollutants (PAHs, OCPs) in sediments over time in the coastal areas of Mong Cai, Quang Ninh, have been determined.
- Analyzed and predicted the origin and environmental risks in coastal waters of Mong Cai city..

6. Research orientation

6.1. Research orientation on the accumulation characteristics of heavy metals, PAHs and OCPs

- Heavy metals tend to bind to fine sediments and organic matter, while PAHs are mainly adsorbed into the organic phase. Heavy metals have different accumulations in space due to the influence of particle size composition, river flow and coastal currents. According to the accumulation trend over time, the content of heavy metals, OCPs and PAHs can increase or decrease during the period of industrial and agricultural development and due to environmental management policies. Therefore, to analyze the accumulation characteristics of sediments, it is necessary to analyze particle size composition, mineral composition, total organic carbon, pH, Eh; analyze stable isotopes δ13C, δ15N, analyze the radioactive activity of 210Pb and 226Ra. This is to understand environmental conditions, determine sediment age and identify pollution sources over time, support environmental risk assessment and propose management solutions.

- Assess the level of pollution based on analysis and determination of the content in sediment of heavy metals, OCPs, PAHs compounds. Compare the content of heavy metals, OCPs, PAHs with ISQGs standards and with other areas to assess the level of pollution.

6.2. Determining the origin of KLN, PAHs and OCPs

- Heavy metals are often mainly derived from natural and anthropogenic activities such as industry and agriculture. OCPs are derived from agriculture, PAHs are derived from fuel combustion activities. To determine the origin of heavy metals, PAHs, OCPs in sediments, it is necessary to evaluate the correlation between heavy metals, PAHs and OCPs with particle size composition, with total organic carbon; the correlation between heavy metals and persistent organic substances to clarify the link between pollutants; Cluster analysis combined with principal component analysis (PCA) to determine the origin of heavy metals and detect accumulation trends; Determine the origin of PAHs through analysis of the ratio of PAHs from petroleum sources (Petrogenic) and combustion sources (Pyrogenic), the indexes FLR/202 and ANT/178; FLU/(FLU+PY) and ANT/(ANT+PHE); Identify the source of OCPs through analysis of DDT/(DDD+DDE) and DDD/DDE ratios.

6.3. Determining the environmental risks of KLN, PAHs and OCPs

Some heavy metals and persistent organic compounds that exceed the toxic threshold will cause a high risk of ecological degradation. Sediments in estuaries are at higher risk than other places in the region. To assess environmental risks, it is necessary to calculate indicators and coefficients such as the environmental risk coefficient RQ, the metal accumulation index Igeo, the metal enrichment index EF, the contamination index CF, the ecological risk potential, the level of contamination CD, the ecological risk coefficient RI to assess the level of impact and risk to the coastal marine environment of Mong Cai.

7. Thesis structure

The thesis is structured into 4 chapters excluding the introduction, conclusion and references including:

Chapter 1. Overview of the research situation and area.

Chapter 2. Research objects and methods.

Chapter 3. Characteristics of accumulation of heavy metals and persistent organic compounds.

Chapter 4. Sources of heavy metals, persistent organic substances and environmental risks.

Chapter 1. OVERVIEW OF THE SITUATION AND STUDY AREA

1.1. Overview of accumulation characteristics, sources and environmental risks of heavy metals, PAHs and OCPs

1.2. Accumulation of heavy metals, PAHs and OCPs in marine environment in the world and Vietnam

1.2.1. In the world

The main sources of heavy metals are from the mainland to the coast. Studies on OCPs and PAHs in the world have also shown that human impacts have increased over time based on studies near estuaries and the Gulf of Tonkin in China [19-22]. To manage and evaluate human activities, countries around the world have issued indicators and allowable limits of pollutants in the environment. Canada and the United States are two countries that have proposed temporary regulations on environmental quality standards for sediments and organisms both on the mainland and in the sea [54].

1.2.2. In Vietnam

Domestic studies on the current status and evolution of pollution in the marine environment in different areas of Vietnam have shown signs that the content of heavy metals, OCPs, and PAHs exceeds the ISQG level, increases over time, and accumulates strongly in surface sediments and sediment columns. Examples of these areas include the coast of Thanh Hoa, provinces along the Red River, the Ba Lat estuary, the coast of Hai Phong, Quang Ninh, the Can Gio area, and coastal lagoons in the Central region [60-85].

1.3. Natural conditions of the coastal area of Mong Cai City

1.3.1. Geographical location, topography and geomorphology

Geographical location

Mong Cai City has an area of 51,953 ha, bordered in the North by the mainland of Mong Cai City, in the South by the Gulf of Tonkin, in the West by Ha Coi Bay, in the East by the Ka Long River mouth, and the border between Vietnam and China [86].

Topography and geomorphology

Mong Cai has a mountainous and midland coastal terrain, located in the Dong Trieu -Mong Cai arc, forming 3 distinct regions: the northern mountainous region, the coastal midland region and the Southern island region [87].

1.3.2. Climate and river characteristics

Mong Cai's climate is relatively mild, tropical monsoon, hot and humid, with heavy rain; there are 2 main types of wind: northeast wind and southeast wind; storms occur from May to October [87].

1.3.3. Tidal regime, river characteristics

The coastal area of Mong Cai has an irregular tidal regime [89]. Mong Cai City has 3 main rivers: Ka Long River, Trang Vinh River, and Pat Cap River, and small streams with large slopes and short flows.

1.3.4. Natural resources

1.3.4.1. Land resources

The coastal area of Mong Cai City has a total surveyed area of 51,953 hectares with 11.8% agricultural land, 55.3% forestry land, 6.3% specialized land, and 1.3% residential land [80], including 6 main soil groups: sandy soil (C), saline soil (M), acid sulfate soil (S), alluvial soil (P), soil with mottled clay layer (L), and grey soil (X) [87].

1.3.4.2. Water resources

The total water of Mong Cai City is 965.05 million m^3; the amount of water that can be exploited and used is only about 841.82 million m^3; the amount of water that can be allocated is 748.24 million [91].

1.3.4.3. Forest resources

Mong Cai has forest resources with a fairly rich vegetation. In the city, there are thousands of hectares of mangrove forests assigned to forest owners for management and protection.

1.3.4.4. Marine resources

With a 50 km long coastline, a large sea area, and a large tidal flat area. Aquaculture area of 2,172.3 ha. Aquaculture output of 16.3 thousand tons [91].

1.3.4.5. Mineral resources

Mong Cai City has the main types of minerals, which are construction material minerals scattered throughout the city, specifically including glass sand, titanium (ilmenite) mineral placer, brick and tile clay, granite paving stone, and construction sand and gravel [84].

1.4. Socio-economic characteristics of the coastal of Mong Cai City

1.4.1. Population and society

The population of Mong Cai City in 2020 was 109.4 thousand people, including 5 ethnic groups: Kinh, Dao, Tay, Hoa, and San Diu. Mong Cai includes 17 commune-level administrative units (8 wards and 9 communes) [89].

1.4.2. Economic situation

Mong Cai has a Bac Luan international border gate and several small-scale border gates. Industrial activities in Mong Cai City are quite vibrant (including Vietnamese and Chinese enterprises), notably Hai Yen Industrial Park, with polluting production sectors including consumer goods production, textiles, installation, precision mechanics, construction materials, etc. Agricultural activities are substantial in Mong Cai and the vast mainland side of China. In recent years, fishery production has been a key economic sector in the city's socio-economic development strategy and has been developed in-depth, providing products for domestic and export needs.

1.5. Affecting sources to the coastal environment of Mong Cai city

Sources affecting coastal sediments of Mong Cai City include tourists, residential activities, industrial park activities, agriculture, and aquaculture, which will create greater pressure on the environment with waste.

Chapter 2. OBJECTS AND METHODOLOGY

2.1. Research objects

The research objects are 12 heavy metals, 7 PAH compounds, 10 OCP compounds in surface and core sediments in the coastal area of Mong Cai City.

The extended research objects include grain sizes, total organic carbon (TOC), mineral composition (quartz, illite, kaolinite, feldspar, chlorite, goethite, gibbsite), radioactive isotopes (^{226}Ra, ^{210}Pb), and stable isotopes (δ^{13}C, δ^{15}N).

2.2. Research scope

The spatial scope is the coastal area of Mong Cai city from the coast stretching to the sea with a depth of 10m.

Sampling locations in the coastal area of Mong Cai were taken in March 2020, including 22 locations, of which 20 surface sediment samples and 2 core samples. The location of stations was determined using GPS-Map 78S (Garmin) (Figure 2.1).

The surface sampling locations ensure coverage of the coastal area of Mong Cai city. Two cores are distributed in two representative locations: one core is distributed at the edge of the mangrove forest near the border, and the other is arranged in Ha Coi Bay. The study collects data on grain sizes, pH, Eh, mineral compositions, heavy metals, radioactive isotopes, TOC, stable isotopes, PAHs, and OCPs. Samples collected surface sediment samples at 20 locations, totalling 104 samples of 6 parameters. The C1 sediment core collected 121 samples of 6 parameters. The C2 sediment core collected 99 samples of 6 parameters.

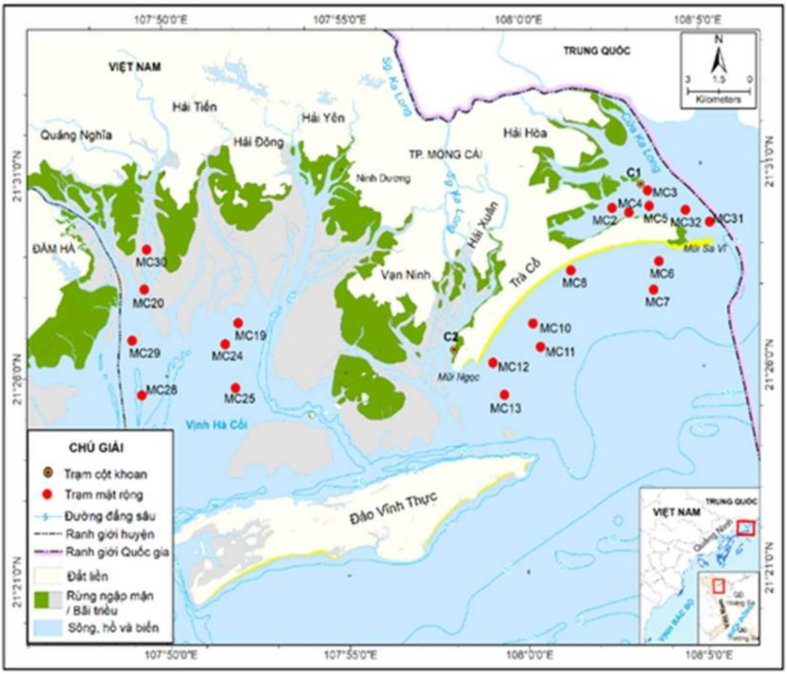


Figure 2.1. Sampling location

2.3. Approaches

The thesis used 5 approaches including: inheritance, system, interdisciplinary, model, and direct.

2.4. Methods

2.4.1. Preliminary treatment of samples and sample containers

Samples are contained in PP plastic tubes with caps of about 50 ml capacity, PP tubes are treated before being used.

2.4.2. Field methods

2.4.2.1. Sediment sampling at sampling points

Surface sediments were collected using a Petersen grab. Core samples were collected using a manual piston core, the tube made of Plexiglass. Surface sediments were taken 0-5 cm. Core samples were cut into appropriate thick layers to the end of the sediment column. All surface samples and core samples were stored at 4^0C in ice boxes until they were returned to the laboratory [969.

2.4.2.2. pH and Eh measurements

Rapid pH and Eh parameters of sediments were measured directly in the field using an Oakton 110 pH meter to determine environmental conditions, thereby assessing the behavior of pollutants in the environment.

2.4.3. Laboratory analysis methods

At the laboratory, they were analyzed for grain sizes, TOC, minerals, radioactive isotopes, stable isotopes, and heavy metals, OCPs and PAHs.

Grain size analysis

Grain sizes were analyzed by pipette [99] and sieves at the laboratory of the Institute of Marine Resources and Environment.

Method of mineral composition analysis

Mineral composition analysis was performed on an X-ray diffractometer (D8 Advance) using Cu (Kα1,2) radiation. The settings included a voltage of 35 kV, a current of 35 mA with a step of 0.015°2Θ, a dwell time of 3 s, and a scanning range of 5 ÷ 60 °2Θ [103].

Total organic carbon analysis

Total organic carbon (TOC) was analyzed at the laboratory of the Institute of Marine Resources and Environment. TOC content in sediments was determined by potassium dichromate ($K_2Cr_2O_7$) [104].

Stable isotope analysis

The δ^{13}C and δ^{15}N in sediments were analyzed on an EA-IRMS isotope ratio mass spectrometer (UK), PDZ Europa 20-20 system of Sercon, Cheshire, UK. This analysis was performed at the Institute of Nuclear Science and Technology in Hanoi.

Radioactive isotope analysis

Radioactive isotopes ^{210}Pb and ^{226}Ra in sediment samples were analyzed [105] at the Laboratory of the Institute of Nuclear Research in Da Lat.

Chronology model: Calculated by the CRS model [106-108].

Heavy metal analysis

Sediments after being pre-treated will be digested at the Institute of Marine Resources and Environment. Then analyzed for heavy metals on ICP-MS [109] at the University of Natural Sciences, Hanoi.

Analysis of persistent organic pollutants

PAHs and OCPs were analyzed by Agilent 5977 GC/MS [112] using Agilent HP-5MS UI column chromatography (30 m x 0.25 mm; 0.25 µm).

2.5. Quality standards, environmental risk assessment indicators

2.5.1. Canadian sediment quality standards thresholds

Sediment quality is assessed according to the Canadian interim marine sediment suality guidelines with ISQG thresholds (unaffected organisms) and PEL thresholds (affected organisms) [54].

2.5.2. Pollution assessment indices

Heavy metals pollution indices were assessed include geoaccumulation (Igeo) [113], enrichment factor (EF) [55], contamination factor (CF), contamination degree (CD) [56], ecological risk potential (ER), ecological risk (RI) [56]. Risk quotient *(*RQ) [114] for both metals and persistent organic pollutants.

2.6. Indicators, origin

2.6.1. Identifying the origin of organic matter

Identify the origin of organic matter through 2 parameters: $\delta^{13}C$ [116] and $\delta^{15}N$ [117].

2.6.2. Identifying the origin of heavy metals

Identify the origin of heavy metals through correlation analysis, principal components and clustering.

2.6.3. Identifying the origin of PAHs

Based on 2 pairs of ratios: FLU/(FLU+PY) [118] and ANT/(ANT+PHE) [118]; FLR/202 and ANT/178 [119].

2.6.4. Identifying the origin of OCPs

Based on the ratios DDT/(DDD+DDE), DDD/DDE [120].

2.7. Data analysis, statistical processing, graph, and maps

Sediment parameters included in the calculation include grain size, minerals, heavy metals, persistent organic pollutants, and TOC.

Data processing analysis includes correlation analysis, maximum value, minimum value, average value, cluster analysis, and principal component analysis. These analyses are performed on Origin Pro 2021 software.

Graphs and maps using Sigmaplot and ArcGIS software.

Chapter 3. CHARACTERISTICS OF ACCUMULATION OF HEAVY METALS AND PERSISTENT ORGANIC POLLUTANTS IN SEDIMENTS

3.1. Distribution of grain size, pH, Eh and minerals

3.1.1. Distribution of grain size

The Mong Cai coastal area had 6 types of sediments: coarse sand, medium sand, fine sand, very fine sand, very coarse silt, and coarse silt. The surface sediment was common fine sand, followed by very fine sand, then coarse sand, and medium sand. In C1, very fine sand was dominant; in C2, very coarse silt and coarse silt were common.

3.1.2. pH and Eh of sediments

The pH value of sediments ranged from 6.70 ÷ 7.67 and averaged 6.95. The redox potential (Eh) of sediments ranged from -105.30 to -52.20 mV, with an average of -68.11 mV.

3.1.3. TOC in sediments

The highest TOC content is in core; C2, followed by the surface layer and the lowest in C1. In the surface layer, TOC ranges from 0.12 ÷ 1.21%. In core; C1, TOC content ranges from 0.09 ÷ 0.71%. In core; C2, TOC content ranges from 0.63 to 2.86%.

3.1.4. Mineral composition in sediments

Mineral composition in sediments from high to low content includes quartz, illite, kaolinite, feldspar, chlorite, goethite, and gibbsite, which were 78.1%, 5.6%, 4.0%, 3.6%, 2.7%, 1.5%, and 1.3%, respectively.

3.2. Radioactivity, chronology, and sedimentation rate

In C1, radioactivity of $^{210}Pb_{total}$ ranged from 38.45 ÷ 79.97 Bq/kg. The radioactivity of ^{226}Ra ranged from 23.15 ÷ 44.70 Bq/kg, the chronology was from 1877 to 2019 (142 years) (0-50cm), the sedimentation rate ranged from 0.08 ÷ 1.62 cm.

In C2, radioactivity of $^{210}Pb_{total}$ ranged from 25.22÷46.75 Bq/kg, the radioactivity of ^{226}Ra ranged from 29.05÷58.54 Bq/kg. The chronology of C2 (0÷14cm) was 75 years, the sedimentation rate ranged from 0.07÷0.51 cm/year.

3.3. Characteristics of heavy metal distribution and accumulation

3.3.1. Heavy metals in surface sediments

Heavy metals including Fe, Mn, Zn, V, Cr, Pb, Cu, As, Co, Ni, Mo, and Cd were analysed and evaluated in Table 3.4. In general, Cu, Pb, Zn, Cr, Cd, and As concentrations in surface sediments were lower than the ISQG threshold, and other heavy metals had no standards.

3.3.2. Heavy metals in sediment cores

In C1, only As had an average concentration higher than ISQG, some high values of Cu exceeded the ISQG threshold, and the remaining heavy metals had concentrations lower than ISQG or had no standards (Table 3.4, Figure 3.14).

In C2, As had an average concentration higher than ISQG, high values of Cu and Pb exceeded the ISQG threshold. Other heavy metals had lower than ISQG or had no standards (Table 3.4, Figure 3.14).

3.3.3. Comparison of heavy metal concentration with other areas

Comparing the Mong Cai coastal area with neighboring areas such as Tien Yen Bay [122], Cua Ong [67], Red River mouth [123], Thanh Hoa coastal area [60], and Cai River mouth [124], the concentration of most heavy metals in surface sediments and C1, C2 were quite low. Compared with the area around China, the heavy metal concetration in sediments surface and 2 cores in Mong Cai were lower.

Table 3.4. Heavy metal content in surface and 2 cores sediments of Mong Cai coastal
(% - Fe; mg/kg – Cu, Pb, Zn, Cd, As, Cr, Co, Ni, Mn, Mo, V; n = samples)

Position	**Level**	**Fe**	**Mn**	**Zn**	**V**	**Cr**	**Pb**	**Cu**	**As**	**Ni**	**Co**	**Mo**	**Cd**
Surface (n = 20)	Min	0.34	34.67	12.81	5.16	3.63	4.48	2.11	2.54	1.76	1.38	0.02	0.01
	Max	1.26	213.76	30.06	17.57	12.18	16.02	8.21	8.90	6.09	3.74	0.24	0.12
	Sd	0.28	56.30	5.56	3.16	2.30	2.95	1.85	1.35	1.18	0.79	0.05	0.03
C1 (n = 28)	Min	0.92	71.62	25.75	12.97	9.77	11.01	6.96	5.09	5.19	2.76	0.12	0.01
	Max	6.45	202.36	67.48	59.34	37.40	28.51	23.24	21.82	15.91	8.86	0.79	0.22
	Sd	1.56	38.65	12.18	11.43	7.04	4.94	4.40	4.43	2.95	1.68	0.14	0.05
C2 (n = 21)	Min	2.14	175.79	39.10	20.22	17.71	19.76	12.26	12.47	7.80	5.18	0.47	0.01
	Max	8.44	426.83	68.87	55.12	44.19	38.01	27.87	29.99	21.03	13.35	2.52	0.18
	Sd	1.88	54.75	9.27	9.41	6.79	5.18	3.57	4.27	3.46	2.16	0.60	0.05
ISQG		-	-	124	-	52.30	18.70	30.20	7.20	-	-	-	0.70
PEL		-	-	271	-	160	108	112	41.6	-	-	-	4.2
Surface Coefficient RQ		-	-	0.15	-	0.14	0.41	0.15	0.58	-	-	-	0.05
C1 RQ Coefficient		-	-	0.33	-	0.39	0.93	0.46	1.73	-	-	-	0.13
C2 Coefficient RQ		-	-	0.46	-	0.66	1.49	0.59	2.79	-	-	-	0.13
Background Value [14]		392	774.60	67.00	97	92.00	28.00	17.00	4.80	47	17.30	1.10	0.09

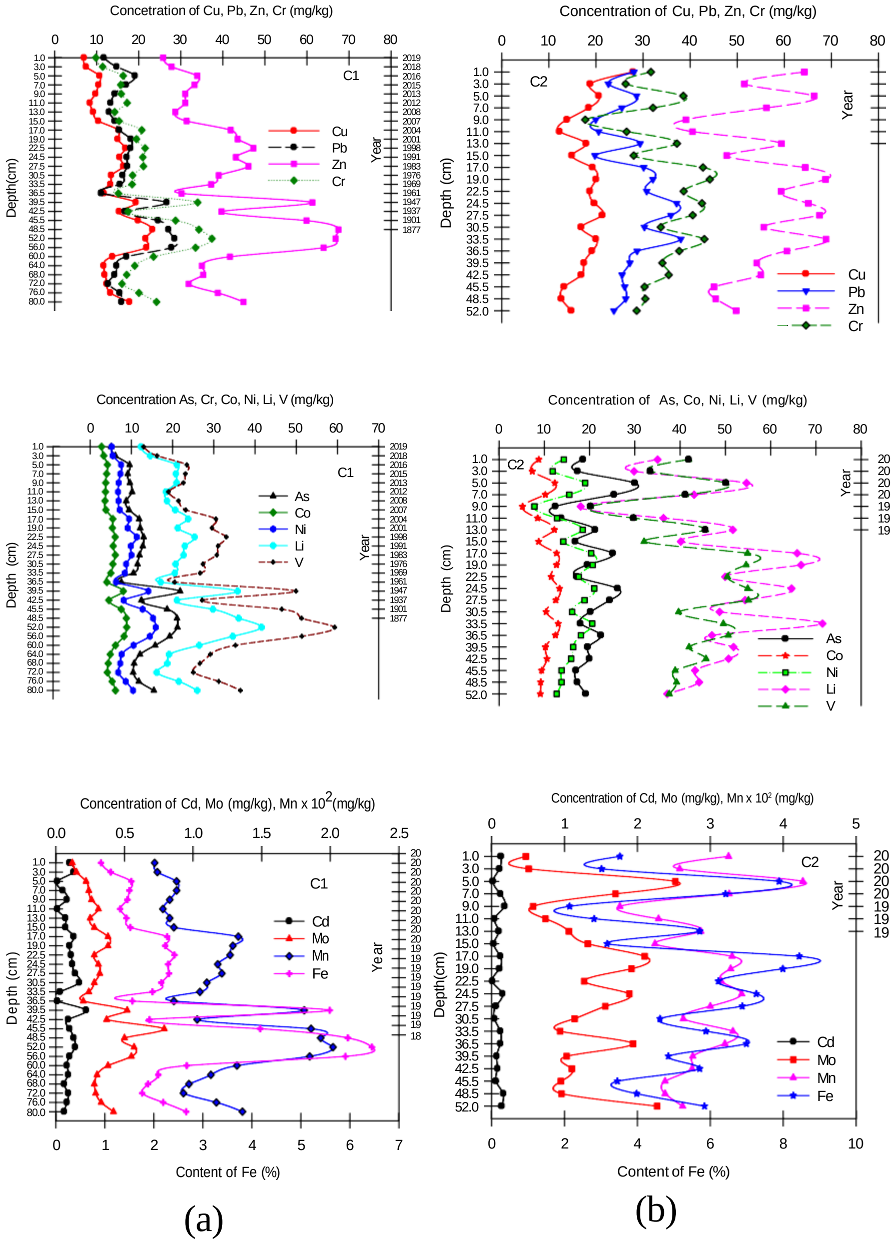
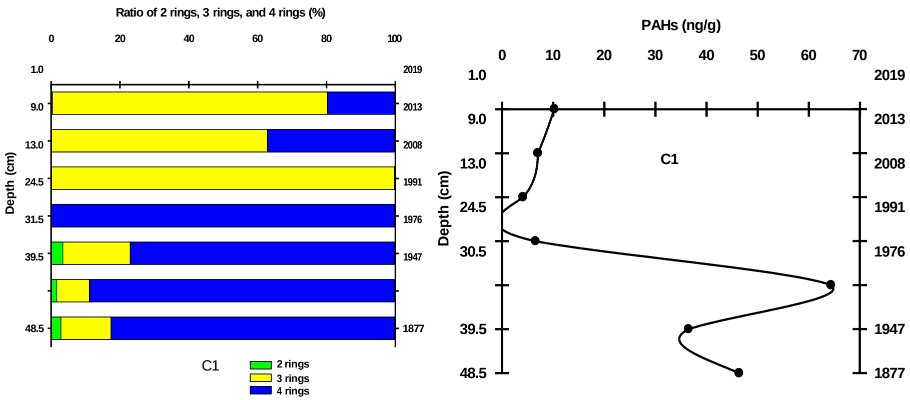


Figure 3.14. Distribution of heavy metals in 2 Cores
(a) – Core C1 (b) – Core C2

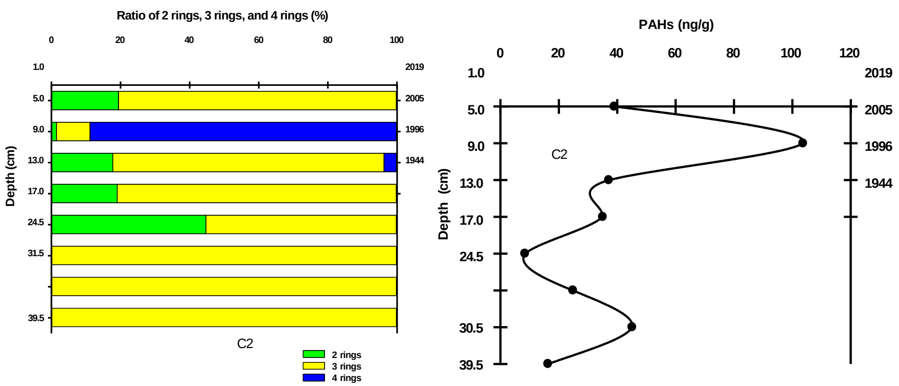
3.4. Characteristics of PAHs distribution and accumulation

3.4.1. Characteristics of distribution and accumulation

The concentration of congener PAHs in the sediment cores didn't have a compound in all of them. The most common compound in C1 and C2 was acenaphthalene. PAH compounds are classified according to a ring structure; 2 rings include NAP; 3 rings are ACE, FLU and PHE; 4 rings are ANT, FLR and PY. In C1, at a depth of 0 ÷ 14 cm from 2008 to 2019, there were mainly 3 rings; at a depth of 23-50 cm from 1877 to 1991, there were mainly 4 rings. In C2, 3 rings dominated in most layers, 4 rings dominated at 4 ÷ 6 cm, and 2 rings dominated at 0 ÷ 18 cm. In general, PAH compounds in both C1 and C2 sediment cores were mainly in the 3- or 4-ring form.



(a)



(b)

Figure 3.15. Distribution of PAHs in the sediment cores

3.4.2. Comparison of PAHs content with other areas

PAH concentrations in the coastal area of Mong Cai were lower than in other areas such as the coastal area of Dong Rui, the lagoons in the central coastal area of Vietnam, the northern area of the Gulf of Tonkin in China, the coast of Malaysia, the bays of Jakarta (Indonesia) and Tokyo (Japan), the coast of Thailand, the coast of Ulsan and Mokpo of Korea, and the coastal areas of Bhavnagar, Sundarban, and Hugli of India. Only the Terengganu area, 5 to 50 km offshore, and on Unguja Island, Tanzania, had a lower concentration of PAHs than Mong Cai.

Table 3.6. PAHs concentration in sediment cores (ng/g)

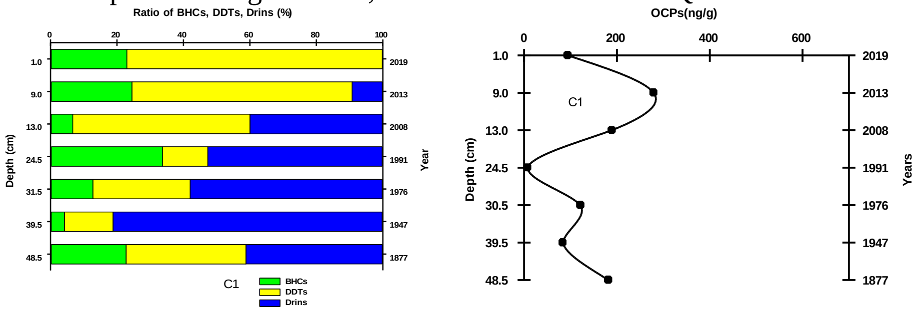
No	Core sedim ennt	Depth (cm)	Year	NAP	ACE	FLU	PHE	ANT	FLR	PY	∑ PAHs
1	C1	0÷2	2019	0.04	4.73	2.48	1.00	1.3	0.71	ND	10.2
2		8÷10	2013	ND	4.40	ND	ND	2.6	ND	ND	7.0
3		12÷14	2008	ND	4.11	ND	ND	ND	ND	ND	4.1
4		23÷26	1991	ND	ND	ND	ND	2.3	2.61	1.55	6.5
5		29÷32	1976	2.21	9.17	3.43	ND	32.6	9.70	7.25	64.4
6		38÷41	1947	0.61	3.45	ND	ND	15.0	10.26	7.18	36.5
7		47÷50	1877	1.32	4.43	2.33	ND	26.8	5.88	5.67	46.4
8	C2	0÷2	2019	7.59	31.45	ND	ND	ND	ND	ND	39.0
9		4÷6	2005	1.50	6.89	3.17	ND	59.8	21.31	11.09	103.7
10		8÷10	1996	6.60	28.55	ND	0.60	1.4	ND	ND	37.1
11		12÷14	1944	6.68	28.32	ND	ND	ND	ND	ND	35.0
12		16÷18	-	3.78	4.67	ND	ND	ND	ND	ND	8.4
13		23÷26	-	ND	24.77	ND	ND	ND	ND	ND	24.8
14		29÷32	-	ND	45.14	ND	ND	ND	ND	ND	45.1
15		38÷41	-	ND	16.26	ND	ND	ND	ND	ND	16.3
ISQGs				34.6	6.71	21.2	86.7	46.9	113	153	
RQ Index core; C1				0.02	0.64	0.06	0.00	0.25	0.04	0.02	
RQ Index core; C2				0.09	3.47	0.02	0.00	0.16	0.02	0.01	

NAP-Naphthalene; ACE-Acenaphthalene; FLU-Fluorene; PHE-Phenanthrene; ANT-Anthracene; FLR-Fluoranthrene; PY-Pyrene; ND–not detection

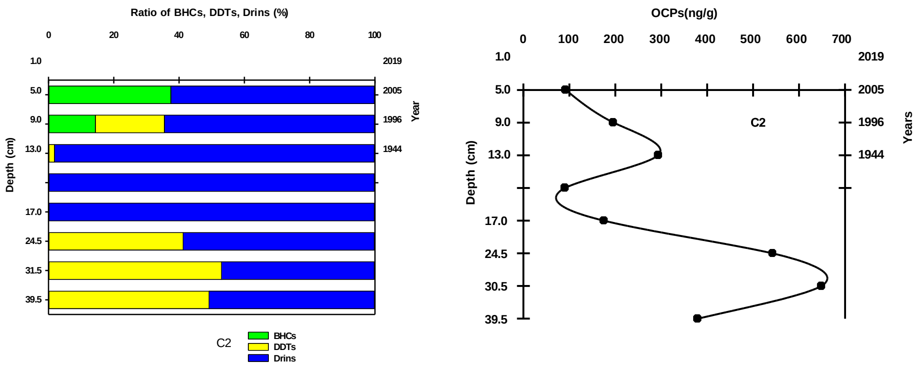
3.5. Characteristics of OCPs distribution and accumulation

3.5.1. Characteristics distribution and accumulation

OCPs compounds appeared with high concentrations in both the surface and deep layers. There were 2 trends;, an increasing trend from 1991 was clearly observed in C1,1 and a decreasing trend from 1996 to 2019 was observed in C2 (Table 3.8). In C1, the total OCPs concentration increased from 1991 to 2013 and gradually decreased in 2019; from 1991 to 1877, the concentration trend gradually increased. In C2, the total OCP concentration gradually decreased with depth and over time. Compared with the Canadian sediment quality standards provisional guidelines, all OCPs exceeded the ISQG level.



(a)



(b)

Figure 3.16. Distribution of OCPs groups and total in sediments

3.5.2. Comparison of OCPs content with other areas

The OCPs content in Mong Cai was higher than other areas in the country [82,83,131] and the coast of China. The nearshore areas, near Mong Cai area such as Nanliu estuary [33], and Saniang Bay [47] near agricultural areas had quite high concentration, while other areas near industrial zones or far from the coast such as the East China Sea, Yellow Sea, Bohai Sea, offshore of the Gulf of Tonkin had lower content.

Table 3.8. Concentration of OCPs in sediment cores

No	Core	Deepth (cm)	Year	BHCs (ng/g)			DDTs (ng/g)					Drin (ng/g)		∑OCPs (ng/g)
				b-BHC	d-BHC	Lindane (g-BHC)	o,p' DDD	p,p' DDT	o,p' DDT	p,p' DDE	o,p' DDE	Aldrin	Dieldrin	
1	C1	0-2	2019	7.4	ND	14.2	11.5	56.9	4.0	ND	ND	ND	ND	94.0
2		8-10	2013	8.4	44.3	15.7	184.8	ND	ND	ND	ND	6.9	18.8	279.0
3		12-14	2008	12.7	ND	ND	100.7	ND	ND	ND	ND	33.4	42.1	188.9
4		23-26	1991	2.5	ND	ND	1.0	ND	ND	ND	ND	1.4	2.5	7.4
5		29-32	1976	15.5	ND	ND	35.5	ND	ND	ND	ND	21.8	48.5	121.3
6		38-41	1947	3.5	ND	ND	12.2	ND	ND	ND	ND	23.1	44.6	83.4
7		47-50	1877	41.2	ND	ND	64.9	ND	ND	0.5	ND	27.2	47.4	181.2
8	C2	0-2	2019	ND	ND	34.5	ND	ND	ND	ND	ND	19.8	37.7	92.0
9		4-6	2005	28.1	ND	ND	41.4	ND	ND	ND	ND	40.8	85.4	195.7
10		8-10	1996	ND	ND	ND	5.5	ND	ND	ND	ND	139.6	148.6	293.6
11		12-14	1944	ND	ND	ND	ND	ND	ND	ND	ND	43.5	46.8	90.3
12		16-18	-	ND	ND	ND	ND	ND	ND	ND	ND	93.1	82.2	175.3
13		23-26	-	ND	ND	ND	64.5	42.3	ND	18.3	98.6	95.6	223.0	542.4
14		29-32	-	ND	ND	ND	38.5	258.2	ND	13.5	33.9	100.1	204.7	648.8
15		38-41	-	ND	ND	ND	20.7	102.1	ND	ND	63.8	48.0	144.6	379.2
ISQGs				-	-	0.32	1.2	1.19	1.19	2.07	2.07	-	0.71	-
RQ Index Column C1				-	-	13.35	48.88	6.83	0.48	0.03	ND	-	41.03	-
RQ Index Column C2				-	-	13.48	17.77	42.29	-	1.92	11.85	-	171.30	-

3.6. Correlation between sediment parameters

3.6.1. Correlation between grain size, minerals, and heavy metals

Surface sediments

Surface sediments had a positive correlation between heavy metals and silt, clay except As, Cd, Mn; and a negative correlation between gravel, sand and heavy metals. The positive correlation between minerals (Kaolinite, Chlorite, Illite) and heavy metals reflected the adsorption nature of minerals and indicates that they are naturally sourced from the continent. The positive correlation between TOC and heavy metals reflects the source of organic matter capable of adsorbing heavy metals. Some non-significant correlations such as Cd, As with grain size and minerals reflected that they were received from other sources (fertilizers and other agricultural chemicals).

C1 core sediments

In C1, the negative correlation between sand and heavy metals reflected the sand content that control the accumulation of most heavy metals. Positive correlations between the heavy metals with each other and with the fine particle sizes (silt and clay) indicate natural sources of supply, while Cd has no correlation with the particle sizes (sand, silt and clay) indicating other sources of supply independent of natural sources. TOC has no relationship with the heavy metals and grain size, indicating that they are local or nearby sources.

C2 Core sediments

In C2, negative correlations were shown between sand and heavy metals and positive correlations between heavy metals and between heavy metals and silt and clay. The sand, silt and clay influenced the accumulation of heavy metals as shown by negative and positive correlations. TOC influenced the accumulation of metals Pb, Cr, Co, Ni, and V. While only Cd had no correlation with other heavy metals reflecting other sources of supply, the remaining heavy metals had positive correlations with each other, indicating the same origin. TOC and silt and clay influenced the accumulation of some heavy metals Pb, Cr, Co and V.

3.6.2. Correlation between grain sizes with PAHs and OCPs

In C1, the sand, silt and clay had weak correlations with OCPs and PAHs through low and insignificant correlation coefficients with most substances. However, only sand, silt, and clay had high and medium correlation coefficients reflecting environmental dynamics; the only significant correlation was between clay and p,p'DDE in C1.

In C2, there was a negative correlation between sand and silt and clay. There was a positive correlation between silt and clay, and between sand and PHE. Silt and PHE were shown to have a negative correlation. TOC showed a negative correlation with NAP while showing a positive correlation with dieldrin, o,p'DDE, p,p' DDT. Among PAH compounds, there is a positive correlation between FLU with PY, FLR, ANT, indicating that the substances have the same origin or are products of transformation from the same type of compounds. In C2, the negative correlation between NAP with dieldrin, o,p'DDE, o,p'DDD reflects the difference in environmental conditions. Between PAH and OCP compounds were independent of grain size (sand, silt, clay) in both C1 and C2, except for PHE which is positively correlated with sand in C2; a positive correlation exists between PAHs and OCPs in C1, between PHE and p,p' DDT, o,p' DDT, between FLU, ANT, FLR and b-BHC in C2.

3.6.3. Correlation between heavy metals with PAHs and OCPs

C1 sediment core

In C1, FLR is positively correlated with Cd, between PY with Pb, Zn, Cd, As, Co and Mn, between ANT, b-BHC, p,p'DDE, Aldrin, Dieldrin with heavy metals (Figure 3.12a). The source of Cd in column C1 is related to the source of PAHs (FLR and PY), other metals Pb, Zn, As, Co, Mn besides natural sources, they also have additional sources with PY.

C2 sediment core

In C2, only Cu is positively correlated with Lindane, showing that they have the same source. The remaining negative correlations between PHE with Zn, Pb, Cr, Co, Ni, Mn, and V; between Cu and Aldrin; reflect unfavorable for the accumulation of metals and organic compounds together.

Chapter 4. ORIGIN OF HEAVY METALS, PERSISTENT ORGANIC POLLUTANTS AND ENVIRONMENTAL RISKS IN MONG CAI COASTAL

4.1. Grouping and characteristics of groups

Result of cluster analysis determine the similarity between pollutants or sediment compounds classified into a group, each group has different characteristics.

4.1.1. Heavy metal groups and characteristics of groups

According to the clustering results, sediment samples are divided into 3–4 groups. In the surface sediments, they were divided into 3 groups. In C1 core, they were divided into 3 groups. In C2 core, they were divided into 4 groups. Sediment parameters are divided into 3 groups. In the surface sediment, they were divided into 3 groups, group 1 was gravel and Mo, group 2 was clay and heavy metals, group 3 was sand. In C1 core, they were divided into 3 groups: group 1 was sand, group 2 was silt, clay and heavy metals, group 3 was TOC. In C2 core, they were divided into 3 groups: group 1 was sand and Cd, group 2 was silt and the remaining heavy metals, group 3 was clay and TOC.

4.1.2. Persistent organic pollutants groups in sediment cores and their characteristics

Based on cluster analysis, 3 sediment groups were divided according to the difference in content and parameters. Group 1 accounted for 11/15 samples with similar sand and silt content but low TOC and OCPs content. Group 2 accounted for 3/15 samples with higher silt, clay, and TOC content than group 1, without some pesticides. Group 3 had 1/15 samples with high sand and TOC content, the highest being Aldrin, Dieldrin, p,p'DDT, and p,p'DDE.

Sediment parameters were divided into 3 groups characterized by 3 types of relationships: group 1 with strong dynamic characteristics, group 2 with a chemical dependence relationship, and group 3 with a relationship with quiet environment by silt and clay.

4.2. Factors controlling pollutants in sediments

4.2.1. Factors controlling heavy metals

By principal component analysis (PCA), there were 3 PCA control sediment characteristics from 6.43% to 59.69% in the surface sediment, from 5.35% to 80.0% in C1 and from 8.15% to 60.07% in C2. In the surface sediment, clay affect and control heavy metals, in C1 core, sand and silt affect Cd, in C2 core, sand, silt and clay affected Cu, As, Pb, Cd, Mn.

4.2.2. Factors governing persistent organic pollutants

PAHs and OCPs had 4 principal components controlling sediment characteristics from 7.55% to 39.89% in C2 and from 9.68% to 44.46% in C1. In general, the grain sizes (sand, silt and clay) governed persistent organic compounds such as NAP, ANT, FLR, PY, Lindane, Aldrin, Dieldrin, ACE, b-

BHC, d-BHC, p,p' DDE in C1. While in C2, only PHE, o,p'DDD, p,p'DDT, Aldrin, Dieldrin compounds are governed by the sand, silt, and clay.

4.3. Origin of heavy metal and persistent organic pollutants

4.3.1. Stable isotope distribution in sediments

Stable isotopes in surface sediments were only analyzed at stations MC2, MC3, MC10, and MC30. The $\delta^{13}C$ values in surface sediments indicated the origin of marine algae (MC10) and terrigenous (MC2, MC3, MC30). The $\delta^{15}N$ values in surface sediments reflected marine sources at MC2, MC3, MC10, and MC30.

4.3.2. Origin of heavy metals in sediments

The origin of heavy metals in sediments was shown through correlation and principal component analysis. In general, heavy metals in sediments are supplied from natural sources that play a major role in the Mong Cai coastal area. Sources from agricultural activities have provided the surface sediment and C2 core.

4.3.3. Origin of PAHs and OCPs accumulation in sediments

➢ **Origin of PAHs**

Based on the ratios of PAHs, it is possible to determine the origin of PAHs in sediments from the combustion process or from petroleum. In the Mong Cai coastal area, the ratio pairs FLR/202 and ANT/178; FLU/(FLU+PY) and ANT/(ANT+PHE) indicate that they originate from petroleum products and petroleum combustion processes.

➢ **Origin of OCPs**

In C1 in the 0÷2 cm layer, DDT/(DDD+DDE) > 2 shows that DDT still receives the surrounding environment from the erosion and leaching process through the canal system flowing into the Ka Long river mouth. At deeper positions, DDT/(DDD+DDE) < 2 shows that DDT has been decomposed; DDD/DDE > 1 at a depth of 47÷50 cm shows that DDT decomposes under anaerobic conditions. In C2, before 1944, DDT/(DDD+DDE) > 2 in the 29 ÷ 32 cm layer shows that DDT decomposition is slow, DDD/DDE < 1 shows that DDT decomposition is under aerobic conditions. Before 2020, Vietnam had not banned the chemicals BHC, DDT, Aldrin and Dieldrin in agriculture, so these chemicals were still present in C2 in the 0 ÷ 2 cm layer (Lindane, Aldrin, Dieldrin), Aldrin and Dieldrin were more common and had higher concentrations in C1. Both Vietnam (2020) and China (2017) banned and restricted the use of BHC, DDT, Aldrin and Dieldrin, so the cumulative concentration of OCPs in coastal areas has been low recently.

4.4. Environmental risks from heavy metals and persistent organic pollutants

4.4.1. Environmental risks from heavy metals

- Risk coefficient of heavy metals

The RQ coefficient of Cu, Pb, Zn, Cd, As, and Cr showed that the surface sediments have no risk of heavy metal pollution; C1 had As at 1.73; C2 had As at 2.79 (Table 3.4).

- Geoaccumulation index (Igeo)

The Igeo showed that most of the surface sediment was at an unpolluted level; in C1, only As was from unpolluted to moderately polluted, and other heavy metals were unpolluted; in C2, Pb and As were from unpolluted to moderately polluted, and the remaining heavy metals were unpolluted (Figure 4.7).

- Enrichment factor (EF)

The EF of Cu, Cr, Co, Ni, Mn, Mo, V showed not enriched in the surface , in C1 and C2. At the low enrichment in the surface sediment (Pb, Zn, Cd), in C1 (Pb, Zn, Cd), in C2 (Pb). At the moderate enrichment, As were in both C1, C2 and in the surface.

- Contamination factor (CF)

The CF in the surface sediments was at low contamination. Medium contamination in C1 (As, Cd) and, in C2 (Pb, Cd, Fe, Mo). Considerable contamination As in C2.

- Ecological risk potential (ER)

The ER of Cu, Pb, Zn, Cd and Cr was low risk in both the surface sediment and cores. Only As in C2 has a medium risk.

- Contamination degree (CD)

The CD in the surface sediment was low, medium contamination in C1, and considerable contamination in C2.

- Ecological risk (RI)

The RI in both the surface sediment, C1 and C2 cores was low. RI of the surface $<$ C1 $<$ C2.

4.4.2. Environmental risk from persistent organic pollutants

For PAH compounds, RQ of C1 showed that C1 has no contamination, and C2 has only ACE at a high risk level, causing ecological impact (Table 3.6). For OCP compounds, RQ showed that C1 had a high pollution of OCPs and very high pollution of OCPs with Dieldrin at 171.3 (Table 3.8). In general, both C1 and C2 had high pollution of OCPs, causing ecological impacts.

4.5. Solutions to prevent heavy metal and persistent organic pollution

To respond to and prevent heavy metal, PAHs, and OCPs pollution in the Mong Cai coastal area, it is necessary to implement the following synchronous measures:

- Limit the disturbance of sediments in deep layers to avoid OCPs pollutants being released back into the environment, affecting organisms due to persistent organic pollution in C1 and C2, which are often in deep layers.
- Further control of waste sources from Hai Yen industrial park; agricultural production, aquaculture, waste from ships and safe waste treatment; Monitoring and early warning of possible environmental risks; restoring and protecting marine ecosystems; Developing and applying clean technology and alternative technology.
- Raising community awareness and corporate responsibility; Strict law enforcement and supervision; International cooperation.

CONCLUSION AND RECOMMENDATIONS

➢ ***CONCLUSION***

1. The coastal area of Mong Cai city has fine to very fine sand sediments distributed predominantly in the shallow coastal waters of the study area. Medium and coarse sand sediments are widely distributed in the Ha Coi Bay river area. The mineral composition in the sediments ranges from high to low including quartz > illite > kaolinite > feldspar > chlorite > goethite > gibbsite. The sediment age shows an average sedimentation rate of 0.08–1.62 cm/year (C1) and 0.07–0.51 cm/year (C2).
2. The heavy metal content is generally lower than the ISQG threshold, increasing gradually from the surface layer to column C2. Column C1 shows a decreasing trend over time, while C2 has an increase in Cu, Pb, Zn, Cr, Co, Ni, Mn from 1996 to 2019, reflecting the impact of human activities.
3. OCPs have concentrations exceeding the ISQG threshold and decreasing

over time, while PAHs are below the threshold but increasing.

4. Isotopes $\delta^{13}C$ and δ^{15} N show that the source of organic matter is mainly a mixture of marine and continental. Heavy metals are mainly natural, but in the surface layer and column C2 there is an agricultural influence. PAHs are of petroleum origin; OCPs are from eroded agricultural soils. In C1, OCPs are also recently added and degrade poorly in the deep layer; in C2, DDT degrades slowly from before 1944.

5. Risk assessment shows that KLNs are mainly at low to medium levels, with As (C1) and Pb, As (C2) at high levels. PAHs are mainly low risk, except for ACE at high levels in C2. OCPs in both columns are at high risk levels, posing potential risks to the ecological environment.

➢ ***RECOMMENDATIONS***

- The study shows that some locations tend to accumulate higher levels of pollutants, especially at the Ka Long estuary and near urban areas. Therefore, it is necessary to establish a long-term monitoring program and expand the survey scope to neighboring areas (e.g. Hai Ha and Tien Yen coastal areas) to have a more comprehensive view of the pollution trend in the Northeast coastal area.

- To fully assess environmental risks, bioassay and benthic biodiversity indicators should be combined to determine the actual level of impact on marine life and sediment ecosystems.

NEW CONTRIBUTIONS OF THE THESIS

- The distribution and accumulation characteristics of heavy metals and persistent organic pollutants (PAHs, OCPs) in sediments over time in the coastal area of Mong Cai, Quang Ninh have been determined.

- Analyzed and predicted the origin and environmental risks in coastal waters of Mong Cai city.

LIST OF THE PUBLICATIONS RELATED TO THE DISSERTATION

1. **B. T. T. Loan**., N. H. Hoang., N. M. Luu., L. V. Nam., P. T. Dung., N. D. Ve., L. N. Sieu, D. H. Nhon., T. D. Thanh (2022). Some sedimentary environment characteristics in the Mong Cai Coastal area, Quang Ninh Province, Vietnam. VNU Journal of Science: Earth and Environmental Sciences, 38(1), 57-70.

2. **Loan, B.T.T**., Nhon, D.H., Ve, N.D., Luu, N.T.M., Sieu, L.N., Hue, N.T., Van Vuong, B., Nghi, D.T., Van Nam, L., Dung, P.T., Anh, V.T., Anh, H.L., Dung, N.T.K., Ha, N.M., Van Chien, N., Lan, N.T.H., 2023. Assessment of the distribution and ecological risks of heavy metals in coastal sediments in Vietnam's Mong Cai area. Environmental Monitoring and Assessment 195:164.

3. **Loan, B.T.T**., Hue, N.T., Nam, H., Van Tu, V., Kha, P.T., Dung, P.T., Luu, N.T.M., Roccaro, P., La Rosa, D., Nhon, D.H., 2024. Distribution of Polycyclic Aromatic Hydrocarbons and Organochlorine Pesticides in Two Coastal Sediment Cores in the Mong Cai Area, Vietnam. Innovation in Urban and Regional Planning: Proceedings of INPUT 2023 - Volume 1 (Lecture Notes in Civil Engineering, 467), pp. 478-489.